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Pyrolysis and oxidation reaction of 1,2, dichloroethylene in Ar; Ar and CH4; Ar, CH4 and O2 mixtures

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ABSTRACT

Pyrolysis and Oxidation Reactions of 1,2-Dichloroethylene in Ar ; Ar and CH_4 ; Ar, CH_4 and O_2 Mixtures

by
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The thermal reaction of trans-1,2-dichloroethylene (DCEE) in methane and oxygen mixtures in Ar bath gas has been studied in 10.5 mm I.D. tubular flow quartz reactors at 1 atmosphere pressure, isothermal temperature between 575°C and 1000°C, and times of 0.3 to 2.0 seconds.

The thermal reaction of trans-1,2-dichloroethylene in the gas phase proceeds via unimolecular HCl elimination under the reaction condition of the present experiments. The chain branching C-Cl bond fission reaction is expected to become important at the higher temperature, competing with the HCl elimination.

The decay trans-1,2-dichloroethylene, intermediates and final product distributions varied in the absence and presence of added O_2 and/or CH_4. Increase in O_2 concentration was observed to accelerate reagent loss in the DCEE/CH_4/O_2 system, especially the fuel lean and stoichiometric systems relative to the DCEE/CH_4 system. Major products were C_2H_2, HCCCl, CH_2CHCl, CH_2CCl_2, C_6H_6, CO, CO_2, and HCl in the DCEE/CH_4/O_2 over a wide temperature range. Minor products were C_2H_4, CH_2Cl, CH_2Cl_2, C_2Cl_2, CH_3CCl_3, C_6H_5Cl, $C_6H_5CH_3$.

The extensive experimental data set will be utilized for construction and validation of a mechanism consisting of elementary reactions based on thermochemical principles, Transition State Theory and Quantum Rice-Ramsperger-Kassel (QRRK) analysis.

PYROLYSIS AND OXIDATION REACTION OF 1,2, DICHLOROETHYLENE IN Ar ; Ar AND CH_4 ; Ar, CH_4 AND O_2 MIXTURES

by
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This thesis is dedicated to my father

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CHAPTER 1

INTRODUCTION

Chlorinated hydrocarbons have been widely utilized as plastics, monomers, solvents, pesticides, and other products. Unfortunately, highly chlorinated compounds, which are used materials and unwanted byproducts generated in the the manufacturing process, have also proven to be both potentially toxic and difficult to dispose of <1,2>.

Combustion is a viable option for destroying numerous hazardous wastes. In addition to conserving increasingly scarce landfill capacity, the combustion of these wastes can produce usable energy. They can also be used to convert methane, the major component in natural gas, into more valuable products such as ethylene and acetylene<3>. The benefits of burning of these wastes, however, can be compromised by the emission of undesirable byproducts such as trace amounts of toxic chlorinated hydrocarbons, dibenzodioxins, and dibenzofuran from incinerators Halogenated hydrocarbon emissions are facing increasingly stringent controls due to both regulatory constraints and public concerns. Concerns raised in the community about potential release of toxic substances from incinerators pose one of the major drawbacks to their use<4>.

Chlorinated compounds have long been recognized as hampering hydrocarbon combustion due to their low heats of combustion and their inhibition of the H + O_2 reaction, by channeling H atoms to form HCl, which is a desirable product because it removes the Cl and can be easily neutralized<5>. However, HCl is a relatively reactive molecule because the H-Cl bond strength is slightly less than H_2 and OH and much less than H--OH. That means that hydrogen chloride is not an irreversible storage for chlorine atoms. Instead it can be rapidly destroyed by the radicals that are likely to be present in a reactive system. It can also serve to inhibit combustion through reactions like :

$OH + HCl \rightarrow H_2O + Cl$

which depletes OH needed for CO burnout. Despite these effects, incineration is feasible, since chlorine is a weak inhibitor in comparison with Br and I <6>, so that a high destruction and removal efficiency is achievable<7>.

In the thermal process, the addition of heat to a gaseous system of molecules, causes a steady increase in their average internal energy. The energy of a particular molecule will, however, fluctuate as it gains and loses energy through molecular collisions. In the relatively long intervals between collisions, this energy will be continuously redistributed over the various parts of molecule. A chemical reaction occurs if enough energy properly localized causes the molecule to fragment, or the bond to break<9>.

The pyrolytic process under high temperature environment involves degradation to small and more unsaturated species. At some stage in the decomposition process the unsaturated molecules and radicals undergo combination and addition reaction and begin to condense leading ultimately to highly carbonized structures or soot<8>. In hydrogenolysis hydrogen serves as a source of hydrogen atoms and also functions as a radical buffer. To a large extent, chlorine atoms and radicals are replaced by H atoms. Hydrogen atoms can result in rapid dechlorination. This occurs by addition to carbon double bonds of chlorinated olefins attached to a Cl forming a new C-H bond, which is stronger than the C-Cl bond. The radical resulting from the addition of H atom can now undergo elimination of the Cl to form an olefin, which has had 1 chlorine replaced by a hydrogen<10>.

Under oxidation, the break down process is enhanced, carbon atoms are bonded to oxygen and many of the unsaturated structures have little or no chance to be formed. Furthermore, the oxidation process is highly exothermic in nature. Therefore along with the chain induced decomposition there are sharp increase in the temperature. More radicals are created and the reaction is driven to completion<11>.

The current study presents experimental results from a study on pyrolysis and oxidation of pure trans-1,2-dichloroethylene conducted in a tubular flow reactor of 1.05

cm I.D at 550°C to 1000°C, 1 atmosphere pressure. The experiments generate suitable quantitative data for use in simulated kinetic mechanisms for better understanding the thermal decay behavior of the chlorinated hydrocarbon pyrolysis and oxidation processes. The data will be used to test a detailed reaction mechanism based on fundamental thermochemical and kinetic principles for these systems. A small initial mechanism for DCEE pyrolysis is also presented in this thesis.

CHAPTER 2

PREVIOUS STUDIES

There are few previous thermolytic studies on dichloroethylene in the literature. Only one pyrolysis was studied under low temperature reaction condition below 475°C <12>and a second study examined pyrolysis in the hydrogen <9>. Gooodall and Howlett (1956)<12,13> studied gas phase pyrolysis of the cis and trans isomers of 1,2-$C_2H_2Cl_2$ in a seasoned reaction vessel with static and flow systems between 360°C and 475°C over the initial pressure range 31-478 mm. These DCEE compounds were decomposed to HCl and monochloroethylene, the kinetics of both dehydrochlorinations being identical. They believed that the isomers went molecular elimination of HCl at equal rates and a radical chain reaction mechanism was proposed.

$M + C_2H_2Cl_2 \rightarrow M + C_2H_2Cl_2 + Cl$

$Cl + C_2H_2Cl_2 \rightarrow HCl + C_2H_2Cl_2$

$C_2HCl_2 \rightarrow Cl + C_2HCl$

$M + C_2H_2Cl + Cl \rightarrow M + C_2H_2Cl_2$

Manion et.al<9>examined the thermolyses in hydrogen of 3-6 vol% 1,1-dichloroethene, trans-1, 2-dichloroethene, trichoroethene, and tetrachloro-ethene in a tubular flow reaction at atmosphere pressure between 555°C and 795°C. The major products in the hydrogenolysis of trans-1,2-dichloroethylene were HCl, CH_4, C_2H_2, C_2H_6, C_2H_3Cl. Minor products were C_2HCl_3, C_6H_6, C_6H_5Cl, and the isomers of $C_6H_4Cl_2$, C_6Cl_6, $C_6H_3Cl_3$. They reported that monochloroethylenes and dichloroethylenes, prominent products in the pyrolysis of tran-1,2-dichloroethene were not found and molecular elimination of HCl also occurs but appears to become less important.. They suggested one mode of reaction resulting in the overall net displacement

of chlorine by hydrogen and when this pathway is followed, all substrates will lead to vinyl chloride and ultimately ethene.

$H_2 + M \rightarrow H + H + M$

$C_2H_2Cl_2 + H_2 \rightarrow CH_2CHCl + HCl$

$CH_2CHCl + H \rightarrow CH_2ClCH_2$

$CH_2ClCH_2 \rightarrow C_2H_4 + Cl$

$CH_2CHCl + H \rightarrow CH_3CHCl$

$CH_3CHCl + HCl \rightarrow CH_3CH_2Cl + Cl$

$CH_3CH_2Cl \rightarrow C_2H_4 + HCl$

$CH_2CHCl \rightarrow C_2H_2 + HCl$ (a)

$C_2H_2Cl_2 \rightarrow HCCCl + HCl$ (b)

Manion et.al suggested reaction (b) is slower than (a) because 1.2-$C_2H_2Cl_2$ lacks an unsaturated carbon with a Cl atom. H atom addition to an unsaturated carbon with a Cl bonded to it will always result in β-scission of the C-Cl bond. This led to the absence of HCCCl from the product spectrum. The study of Manion et.al showed reversible conversion to the cis form from the trans form occurs under his conditions.

The photochlorination of pure cis- and trans-1,2-dichloroethylene was studied by Ascough, Cocker and Daniton<14> between 35°C and 65°C in a 5cm I.D cylindrical quartz reaction vessel which was connected to an optical system and to a gas chromatography. They showed that a chlorine atom catalyzed isomerization of cis-$C_2H_2Cl_2$ occured and this competed with the normal addition of chlorine to form tetrachloroethane. The isomerization probably resulted from the decomposition of an energy rich trichloroethyl radical. At first the important propagation reactions were considered. :

$Cl + DCEE \rightarrow C.HClCHCl2*$

$C.HClCHCl_2* + Cl_2 \rightarrow CHCl_2CHCl_2 + Cl$

Specifically the proposed the three possible termination reactions between Cl and ACl :

decomposition : $C.HClCHCl_2^* \rightarrow$ x cis DCEE + (1-x) trans DCEE + Cl

deactivation : $C.HClCHCl_2^* + Cl_2 \rightarrow CHClCHCl_2 + Cl_2$

atom exchange : $C.HClCHCl_2^* +$ DCEE $\rightarrow$ DCEE $+ CHCl_2C.HCl^*$

Knox and Riddick<15>also studied activated trichloroethyl radicals which were produced by the addition of a chlorine atom to 1,2-dichloethene in a 85 cm^3 Pyrex reaction vessel , which is illuminated with light from a 250 W projection lamp for 1-5 minutes, with propane. They found between 35°C and 133°C, $C.HClCHCl_2^*$ decomposes to give 78 % cis-dichloroethene and 22 % trans-dichloroethene.

Atkinson and Aschmann<16> studied the gas phase reactions of Cl atoms with five sets of chloroethenes and ethanes at 298±2 K and 735 torr total pressure in a cylindrical reaction bag surrounded by black lights. They showed that for the 1,2-dichloroethenes the Cl atom reactions are not at the high pressure limits at atmospheric pressure while the reaction of Cl atoms with the chloroethenes are fairly close to the limiting high pressure limits at 735 torr total pressure of air. They report that the formation of trans-1,2-dichloroethylene from the irradiations involving cis-1,2-dichloroethylene was observed, and similarly cis-1,2-dichloroethylene was formed from the Cl atom reaction with cis-1,2-dichloroethylene. They report that these products (cis and trans isomer from parent cis and trans isomer) have the rate constant virtually identical to those for parent cis and trans isomer when these products react with Cl atoms under their conditions.

The homogeneous gas phase reactions the OH radical with the chloroethenes were investigated by Tuazon et.al<17> at 298 ± 2 K and atmosphere pressure, using ethane as a scavenger for chlorine atoms produced in these radical reactions. The reaction of 1,2-$C_2H_2Cl_2$ with OH radicals was observed to be one of the dominant atmospheric loss process. They reported C-C cleavage of the corresponding hydroxydichloroethoxy radical produces HC(O)Cl as well as HO.CHCl and $.CHCl_2$ as major products which were observed by long pathlength FT-IR absorption spectroscopy. They demonstrated formation of Cl from the oxidation of HOCHCl and subsequent Cl reaction with the 1,2-

dichloroethene could explain, in part, the higher HC(O)Cl yields observed in the absence of Cl atom scavengers. They concluded the cleavage of the C-C bond of the $CHCl_2CH(O.)Cl$ radical formed in the Cl atom reaction generates directly one HOC(O)Cl plus another from the subsequent oxidation of the .CHCl2 fragment, which also generates Cl atom to maintain the chain reaction.

Zhang et.al<18> measured the reactions hydroxyl radicals with the three dichloroethenes over the temperature range 240-400 K at total pressure of 35 torr by using the flash photolysis-resonance fluorescence technique. They made general observations about the room temperature rate constants for the reactions of OH with various ethenes : first, the addition of a single chlorine to ethene leads to a small reduction in the OH addition rate constant ; the addition of a second chlorine on the same carbon leads to a rate constant increase above that for ethene. If the two chlorine atoms are on different carbons, however, there is a considerable decrease in the rate constant. Addition of a third chlorine leads to a further small decrease in the rate constant. Finally, for tetrachloroethene, with four chlorine atoms, the rate constant for reaction with OH is about 0.02 times that for ethene.

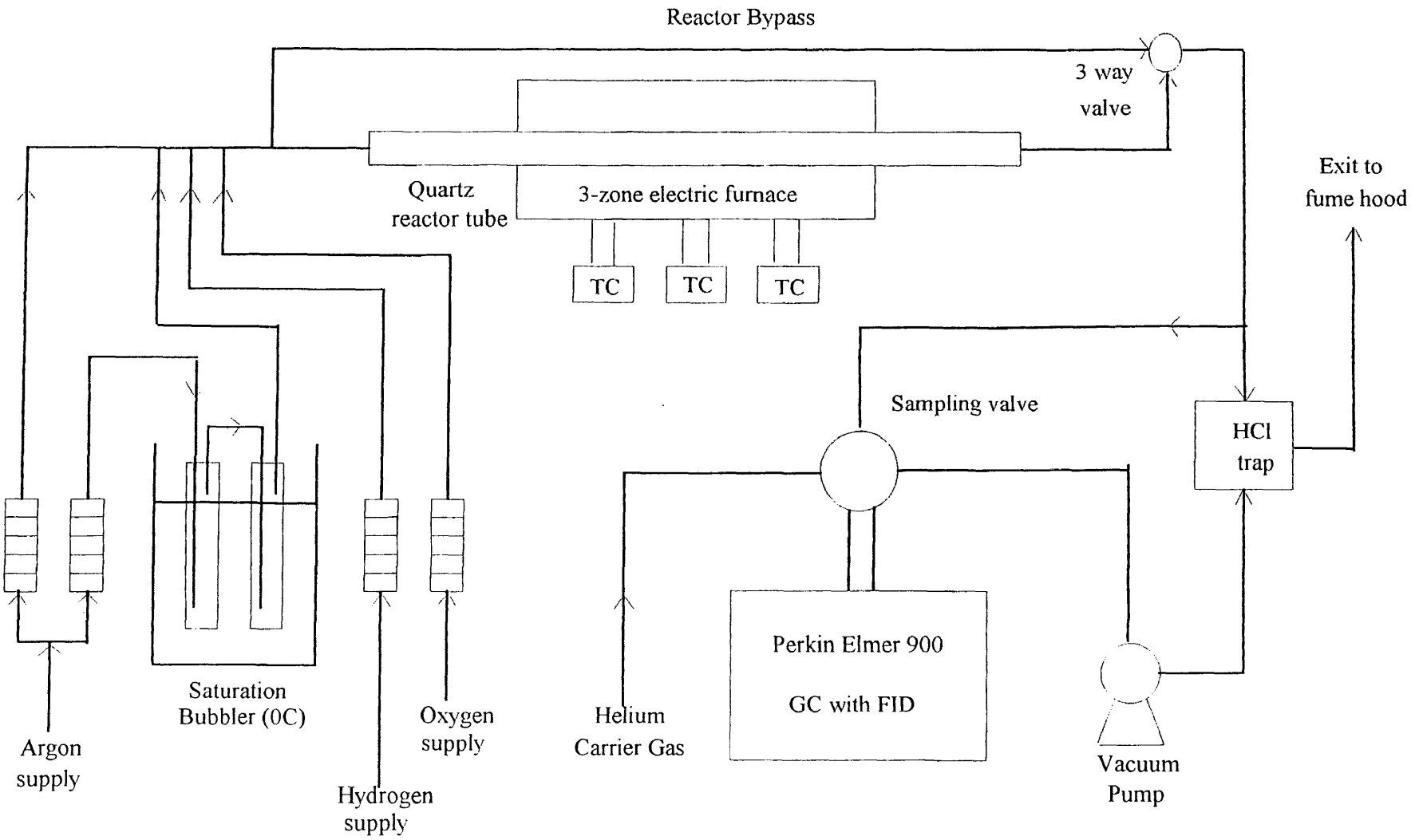

Figure 3.1 Experimental System

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Experimental Apparatus

The thermal reaction of trans-1,2-dichloroethylene (DCEE) in methane and oxygen mixtures in Ar bath gas has been studied in 10.5 mm I.D tubular flow quartz reactor at 1 atmmosphere pressure, isothermal over temperature range from 575°C to 1000°C and a residence time range of 0.3 to 2.0 seconds. The tubular flow quartz tube was housed within a three zone Lindberg electric tube furnace, each zone was controlled separately in order to maintain at a constant temperature.

A diagram of the experimental system is shown in figure 3.1. Carrier gas, Argon, was passed through two saturation bubblers which are kept at 0°C using an ice bath to carry the trans-dichloroethylene through the reactor. A second line of Argon was used as make-up to control the desired mole fraction between reagents. Methane and oxygen were brought into the flow stream as required. The flow rate for each gas was measured with calibrated rotameter and also total flow is composed up of the sum of the flow of each reagent at the desired residence times for each temperature.

Before entering the reactor, the flow mixture was run directly from the bubbler to the GC sampling valve via a by-pass line. This was necessary to determine the GC peak area that corresponded to the input initial concentration of the reagents without going through the high temperature reactor. The reactor effluent gas passed through heated transfer line to the GC sampler and exhaust. The mixture was preheated to about 200°C before entering the reactor to improve isothermal temperature control. All gas line to the analytical equipment were held at about 100°C to limit condensation.

Outlet gases from the reactor were passed to the GC through a short glass tube packed with glass wool, this served as a filter to trap carbon particles, preventing

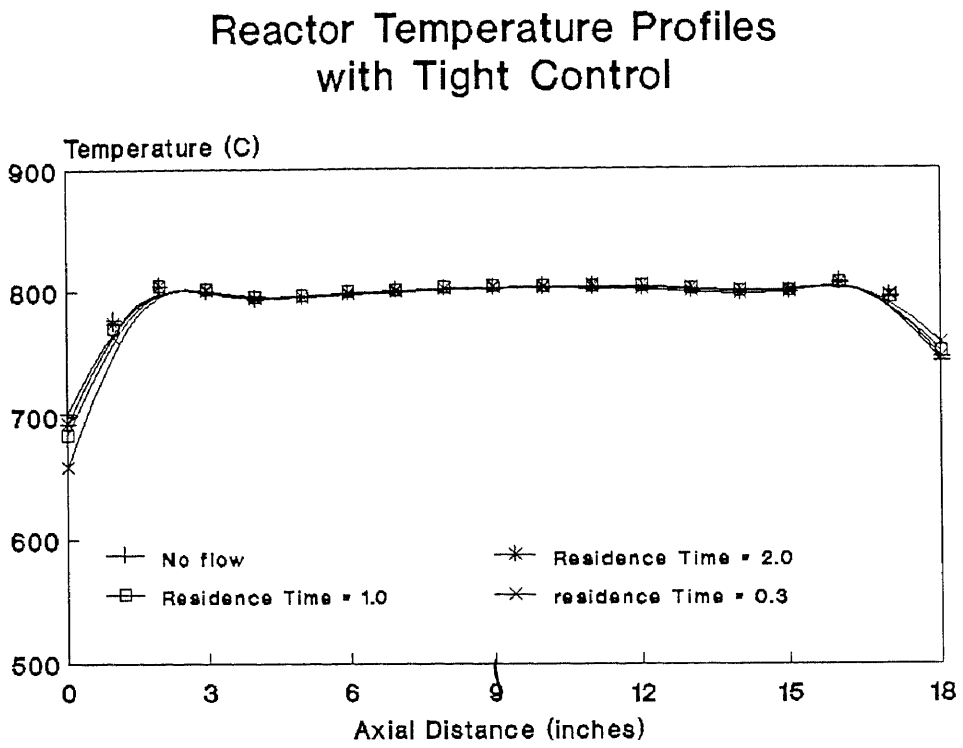

Figure 3.2

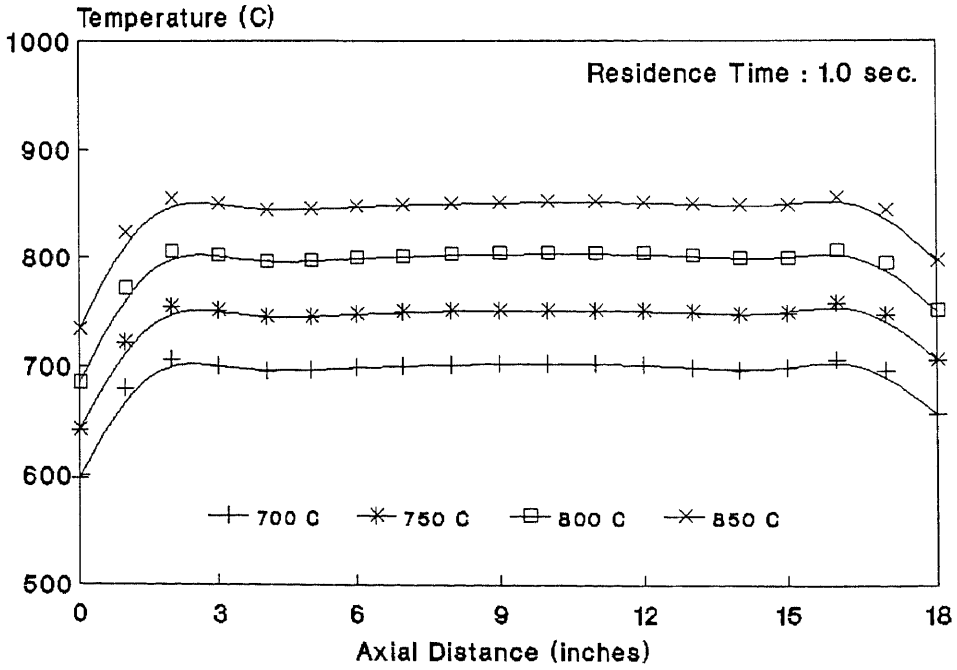

Figure 3.3

contamination of the GC sampling valve. The bulk of the effluent was passed through a sodium bicarbonate flask for neutralization before being released to the atmosphere via a fume hood.

3.2 Temperature Control and Measurement

A 10.5 mm I.D quartz reactor tube was installed in a three zone electric tube furnace 18 inches length with three independent temperature controllers (Omega Engineering, Inc.). The actual temperature profile of the tubular reactor was obtained using K type thermocouple probe which could be moved coaxially within reactor. The temperature measurements were performed with steady flow rate of Argon gas through reactor to determine accurate temperature profile for each residence time and temperature. The good temperature control, which prevented the reactor entrance temperature from dropping with varied flow rates, was required to get isothermal reaction conditions over the control 80 % of the reactor. The temperature profiles are shown in Figure 3.2 were isothermal to within ±5°C for 37 cm for temperature ranges of this study. Figure 3.3 shows isothermal temperature profiles at several temperatures.

3.3 Quantitative Analysis of Reaction Products

A Perkin Elmer 900 gas chromatography with dual Flame Ionization Detector was used on lined to quantitatively determine the concentration of the reaction products. The lines between reactor exit and GC analysis were heated to 100°C to limit condensation. A 1% Alltech AT-1000 on Graphpac GB 60/80 mesh column with 2m length by 1/8" O.D. was used to separate C_2 through C_6 compounds. CO, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 from reactor effluent stream were separated using a carbosphere 80/100 mesh packed column 1.5m length by 1/8" O.D.

A six port gas sample valve (Valco Instrument Co.) with a 1.0 ml volume loop was maintained at 160°C and 1 atm pressure. The integration of the chromatograph was

performed with a Varian 4270 integrators. Table 3.1 shows the retention time of compound and peak identification.

Table 3.1 Average Retention Time

Compounds	Average Retention Time (min.)	
CO		3.31*
CO_2		10.35*
CH_4	1.63	6.68*
C_2H_2	2.08	13.71*
C_2H_4	2.34	15.44*
C_2H_6	2.66	16.96*
CH_3Cl	4.09	
C_3H_4	5.61	
HCCCl	5.92	
C_3H_6 & C_3H_8	6.06	
C_2H_3Cl	7.36	
CH_3CH_2Cl	8.66	
CH_2Cl_2	10.45	
C_2Cl_2	10.92	
C_4H_{10}	11.31	
CH_2CCl_2	12.70	
CH_3CHCl_2	13.29	
c-CHClCHCl	13.80	
t-CHClCHCl	14.17	
$CHCl_3$	14.63	
$CH_2ClCHCl_2$	15.26	
CH_3CCl_3	16.53	
CCl_4	16.88	
C_4H_9Cl	17.95	
$CHClCCl_2$	18.76	
$CH_2ClCHCl_2$	19.20	
C_6H_6	19.28	
C_2Cl_4	24.72	
$C_6H_5CH_3$	27.28	
C_6H_5Cl	30.00	

* Retention Time for carbosphere column.

A catalytic converter which contained 5 % ruthenium on alumina catalyst was employed to increase the accuracy of quantitative analysis for CO and CO_2 and placed

between caborsphere column and flame ionization detector. Separated CO, CO_2 from carbosphere column were then reacted with H_2 in the converter which was maintained at 300°C and reduced into two CH_4 products with different retention time, which can be sensitively detected by the FID.

Calibration of the flame ionization detector to obtain appropriate molar response factors was done by injecting a known quantity of the relevant compound such as CH_4, CO, CO_2, etc., then measuring the corresponding response area. The relative response factor was determined for compound shown in Table 3.2. The sensitivity of flame ionization detector corresponds to the number of compounds is similar, and the response factor of C_2 compounds are nearly twice the response of the C_1 compounds.

Table 3.2 Relative Response Factor (RRF)

Compounds	Relative Response Factor (RRF)
CO	0.97*
CO_2	0.92*
CH_4	1.00
C_2H_2	1.81
C_2H_4	2.10
C_2H_6	1.96
CH_3Cl	1.00
C_3H_4	3.00
HCCCl	1.80
C_3H_6 & C_3H_8	3.24
C_2H_3Cl	2.00
CH_2Cl_2	1.00
C_4H_{10}	4.53
CH_2CCl_2	2.00
c-CHClCHCl	1.90
t-CHClCHCl	1.90
$CHClCCl_2$	2.00
$CH_2ClCHCl_2$	2.00
C_6H_6	6.00
$C_6H_5CH_3$	7.00
C_6H_5Cl	6.00

Corrected area = measured area / RRF

* Relative Response Factor for carbosphere column

3.4 Hydrochloric Acid Analysis

Quantitative analysis of HCl product was performed for reactions at each temperature and each residence time. The samples for HCl analysis were collected independent from GC sampling as illustrated as Figure 3.1 In this analysis, the effluent was bubbled through a two stage bubbler before being exhausted to hood. Each stage contained 20 ml of standardized 0.01 M NaOH. The gas was passed through the stage bubbler until the first stage solution reached its phenolphthalein end point. The time for this to occur was recorded. At this point the bubbling was stopped, the aliquots were combined, and titrated to their end point with standardized 0.01 M HCl. Therefore the HCl concentration produced by reaction was easily calculated.

3.5 Qualitative Analysis of Reaction Products

The analysis of the products were performed on a Hewlett Packard 5988 GC/MS with a 50 m length, 0.22 mm ID methyl silicone capillary column. Evacuated 25 ml stainless steel sample cylinders were used for collection of gas samples at the outlet of the reactor. The sample was then injected into the GC/MS via a six port gas sampling valve. The sample was cryogenically focused inside the GC oven, 20 cm loop at front of GC column, with liquid nitrogen.

3.6 Computer Codes Used for the Modeling

3.6.1 CHEMACT

CHEMACT <19>is a computer code that used the QRRK treatment of chemical activation reactions to estimate apparent bimolecular rate constants for various channels that can results in addition, recombination, and insertion reactions. Since these rate constants depend on both pressure and temperature, it is important that includes the appropriate expression for specific pressure of interest in the modeling calculation.

General sources of input data for CHEMACT :

1. Thermodynamic parameters : enthalpy (H_f), entropy (S_f), and heat capacities (C_p) as a function of temperature for reactants, adducts and products are important for accurate results.

2. Molecular parameters describing the size, collision energy transfer and energy levels of the adduct formed by the initial reaction are also needed. These include the mass, number of vibrational modes of the adduct, Lennard-Jones parameters and geometric mean frequency.

3. The bath gas molecule collision diameter, well depth and average energy transferred are needed.

4. High pressure limit rate constants for adduct formation and various isomerization and dissociation product channel of the adduct are also needed.

3.6.2 DISSOC

Fall-off corrections for regular unimolecular decomposition reactions were made by the unimolecular Quantum RRK method<20>. DISSOC computer code<19> analyzed unimolecular reaction with QRRK analysis for proper treatment of fall-off dependency and estimate apparent unimolecular dissociation rate constants for various unimolecular dissociation channels. Same input data with CHEMACT computer code is required to run DISSOC program.

3.6.3 THERM

THERM is a computer code which can be used to estimate, edit, or enter thermodynamic property data for gas phase radicals and molecules using Benson's group additivity method<21,22>. All group contributions considered for a species was recorded and thermodynamic properties are generated in NASA polynomial format in addition to listing more convenient for thermodynamic, kinetic, and equilibrium calculation.

3.6.4 CPFIT

CPFIT[19] is a computer code that determine geometric mean frequency. It accepts input in the form of heat capacities versus temperature to 1000°C in addition to the number of vibrational modes and the number of internal rotors in the molecule.

3.6.5 THERMRXN

Therm contains a chemical reaction interpreter for calculation of thermodynamic property changes of reaction as functions of temperture. THERMRXN [22] can caculate thermodynamic property changes for a desired reaction or an entire CHEMKIN input file. The thermodynamic properties which are calculated are ΔU_r, $\{\Delta E_r\}$, ΔH_r, ΔS_r, ΔG_r, equilibrium constant (K_c) and A_f/A_r ratio forward to reverse Arrhenius A factors.

CHAPTER 4

RESULTS AND DISCUSSION

The following six reaction ratio sets in Table 4.1 were studied and included oxidative and pyrolytic reaction environments.

Table 4.1 Reactant Ratio Sets

Mole Percent	Fuel equivalence
1. trans-CHClCHCl : CH_4 : O_2 : Ar = 1 : 1 : 2 : 96	2
2. trans-CHClCHCl : CH_4 : O_2 : Ar = 1 : 1 : 4 : 94	1
3. trans-CHClCHCl : CH_4 : O_2 : Ar = 1 : 1 : 6 : 92	0.67
4. trans-CHClCHCl : CH_4 :Ar = 1 : 1 : 98	N/A
5. trans-CHClCHCl : O_2 : Ar = 1 : 4 : 95	1
6. trans-CHClCHCl : Ar = 1 : 99	N/A
7. trans-CHClCHCl : CH_4 : O_2 : Ar = 1 : 1 : 6 : 92	0.67
trans-CHClCHCl : CH_4 : Ar = 1 : 1 : 98	N/A

(The Reaction conditions range from fuel equivalence ratios of 0.2 to 2)

Reactor Temperature (°C) : 575 - 1000.

Effective Reactor length : 37 cm.

Reactor Diameter : 1.05 cm.

Residence Time Range (sec.) : 0.03 - 2.0

Operating Pressure : 1 atm.

The temperature range for each was determined on the basis of the conversion rate of trans-dichloroethylene (DCEE) reagent in the 1.05 cm I.D reactor. Stoichiometric (ratio 2) and fuel lean (ratio 3) had a temperature range from 700°C to 800 °C. Fuel rich (ratio 1) was between 725°C and 850°C. The pyrolysis ratio with methane (ratio 4) had the widest temperature range from 725°C to 1000°C. Oxidation reaction excess O_2 (ratio 5) was examined over the lowest temperature range between 575°C and 675°C. Pyrolysis

experiments (ratio 6) were initiated at 650°C. Experiments starting with pure cis-dichloroethylene reagent were examined at 725°C in ratio 3 and 4.

4.1 Reaction of CHClCHCl in $CHClCHCl/CH_4/O_2/Ar$ Oxidative Pyrolysis

Experimental results on decomposition of 1,2-dichloroethylene in the $DCEE/CH_4/O_2/Ar$ system are shown in Figures included together in section 4.6. Figures 4.9 to 4.18 shows normalized concentration (C/Co) as a function of average residence time for several temperatures studied. Figures 4.19 to 4.22 show dichloroethylene and methane decomposition in different reaction environments at 1.0 of second reaction time.

The 1,2-dichloroethylene consistently decreases with increasing reaction time for all temperatures. For a constant residence time, 1,2-dichloroethylene showed a lower concentration with the increasing temperature in all reaction environments.

1,2-dichloroethylene decomposes more rapidly than methane. In the fuel rich system methane did not completely decay , only 70 % methane conversion was achieved, while 1,2-dichloroethylene was completely converted at 850°C. In the fuel lean and in the stoichiometric systems, methane showed similar decomposition with 1,2-dichloroethylene. The decay rate for 1,2-dichloroethylene and methane both increase, with increasing O_2 levels in oxygen reaction systems.

50 % conversion of parent compound at residence time of 1.0 second is observed at reaction temperature 750°C for fuel lean and stoichiometric conditions, and 775°C for fuel rich in oxygen/methane systems, respectively. In the methane/Ar system 50 % decay of the DCEE was at 825°C but 46 % methane was existed at 950°C. In the reaction of DCEE and oxygen initial reaction was observed at 575°C and 50 % conversion of DCEE occurred at 750°C in pyrolysis system.

4.2 Product Distribution and Material Balance

4.2.1 Product Distribution in $CHClCHCl/CH_4/O_2/Ar$ Oxidative Pyrolysis

Figures 4.25 to 4.40 in section 4.6 present the product distribution as function of temperature at 1.0 second residence time and function of reaction time at 725°C to 775°C. The major products observed over the temperature and reaction time range are listed below.

Major products in $DCEE/CH_4/O_2/Ar$

C_2H_2, HCCCl, CH_2CHCl, CH_2CCl_2, C_6H_6, CO, CO_2, HCl.

Minor products in $DCEE/CH_4/O_2/Ar$

C_2H_4, CH_3Cl, C_3H_4, CH_2Cl_2, C_2Cl_2, CH_3CCl_3, $C_6H_5CH_3$, C_6H_5Cl.

At low temperature CH_2CCl_2 was major product, which decomposed and / or further reacted with increasing temperature. All major products except CH_2CCl_2 increases with increasing temperature to a maximum temperature and then starts to decrease in level above 800°C for 2% O_2, above 750°C for 4% O_2 and below 750°C for 6% O_2 reaction system.

The stable intermediate, HCCCl(Chloro Acetylene) is observed to decay slightly faster than CH_2CHCl(Vinyl Chloride). The formation of CO rises rapidly when the majority of intermediate products start to decrease in level. The formation of CO_2 then rises when the large amount of CO produced starts to convert into final product CO_2. The temperature for conversion CO into CO_2 was observed at 775°C for 4% and 6% CH_4/O_2 systems but was above 850°C for 2% O_2.

Benzene formation is observed over a majority of reaction temperature range ; and formation increases with increasing concentration of C_2H_2 in the fuel rich reaction system. Under fuel rich conditions soot and higher molecular weight compounds were observed ; but thesewere not observed under fuel lean conditions due to high oxygen concentration.

4.2.2 Products Distribution in $CHClCHCl/CH_4/Ar$ Pyrolysis

Figures 4.41 shows the distributions for major and minor products as a function of temperature and reaction time. Figures 4.42 to 4.46 presents the product distribution as a function of residence time at 725°C to 900°C as shown section 4.6.

Major products in $CHClCHCl/CH_4/Ar$

C_2H_2, HCCCl, CH_2CHCl, CH_2CCl_2, C_6H_6, HCl.

Minor products in $CHClCHCl/CH_4/Ar$

C_2H_4, CH_3Cl, C_3H_4, CH_2Cl_2, CH_3CCl_3, $C_6H_5CH_3$, C_6H_5Cl.

At low temperature HCCCl and CH_2CCl_2 are major products. However CH_2CCl_2 starts to decompose at 750°C, HCCCl continues to increase in concentration as the main product until 850°C at reaction time 1.0 second, a result of the initial reaction of 1,2-dichloroethylene being dominated by unimolecular HCl elimination :

$CHClCHCl \rightarrow HCl + HCCCl$

CH_2CHCl is formed by the following reaction seuences.

$CHClCHCl + H = CH_2CHCl$ (domination reaction)

$CHClCHCl + H = CH_2ClCHCl$

$CH2ClCHCl = CH_2CHCl + Cl$

$CHClCHCl + CH_4 = CHCHCl + CH_3Cl$

$CHCHCl + HCl = CH_2CHCl + Cl$

$CHCHCl + CH_4 = CH_2CHCl + CH_3$

$CH_2CCl_2 + H = CH_2CHCl + Cl$

This CH_2CHCl product is however limited by its relatively rapid unimolecular decomposition :

$CH_2CHCl = C_2H_2 + HCl$

At low temperature the concentration of CH_2CCl_2 comes from HCl combination with HCCCl, and HCl loss from CH_3CCl_3 and $CH_2ClCHCl_2$. This will be more clearly illustrated by our modeling studies.

Benzene formation is observed above 750°C and as C_2H_2 concentration increases highly, it is found in higher concentrations. High concentration (5.34% 850°C of benzene implies that the formation of high molecular weight compounds and soot may be occurring at these reaction condition. A dark deposit produced by pyrolysis in the DCEE/CH_4/system in / on the sampling filter that is located just past reactor zone.

4.2.3 Products Distribution in CHClCHCl/O_2/Ar Oxidation

Figures 4.48 to 4.50 shows the distributions for major and minor products as a function of temperature and reaction time.

Major products in DCEE/O_2/Ar

C_2H_2, C_2HCl_3, CO_2, CO.

Major products in DCEE/O_2/Ar

HCCCl, CH_2CHCl, CH_2Cl_2, CH_2CCl_2, C_2Cl_4.

We note that 1,2-dichloroethylene has the impurities, CH_2Cl_2, CH_3CHCl_2, and CH_2CCl_2 at the 1-2% level. C_2H_2, CH_2CHCl, CH_2Cl_2 therefore arise primarily from these impurities.

In this reaction system, without methane, 1,2-dichloroethylene decays faster than any other reaction system in our studies. The concentration of CO increases continuously with increasing temperature. Around 675°C the concentration of CO approaches to 72% when 1,2-dichloroethylene is 99% converted.

4.2.4 Product Distribution in CHClCHCl/Ar Pyrolysis

The decay of CHClCHCl as function and time for this reaction system is presented in Figures 4.51 and 4.52 The experiments for this pyrolysis reaction are only complete from 650°C to 725°C, but we have enough data to know the important initial reaction is unimolicular HCl elimination.

Main products in DCEE/Ar

HCCCl, HCl.

Minor products in DCEE/Ar

C_2H_2, C_2Cl_2, CH_3CCl_3, C_2HCl_3, C_6H_6, $CH_2ClCHCl_3$, $CHCl_2CHCl_2$, C_2Cl_4.

Complete decay for 1,2-dichloroethylene occurs at 800°C for 1.0 second residence time. The formation of HCCCl rises linearly when CHClCHCl decreases, as temperature increases, which indicates HCCCl is the initial stable product in the thermal unimolecular decomposition of CHClCHCl. In this basic reaction ratio we report the HCCCl + HCl reaction pathway for unimolecular dissociation is favored over CHCHCl + Cl, unimolecular Cl loss.

4.2.5 Isomerizaton of trans-1,2-CHClCHCl

Althouh the trans form of 1,2-CHClCHCl was used as a starting compound, reversible conversion this reactant to the cis isomer occurs under our conditions. The observation of isomerization is clearly shown in Figures 4.53 for the DCEE/O_2/Ar sysem relatively low reaction temperatures from 575°C to 675°C. The concentration of cis isomer increases from 575°C to 600°C and then decreases consistent with loss of trans isomer and subsequent reaction (HCl elimination). In the DCEE/Ar system isomerization is observed at 600°C. In DCEE/CH_4/O_2 and DCEE/CH_4 systems isomerization appears around 700° C, The extent of conversion could not be obtained because of other chain branching and loss reactions.

It is worthwhile to compare result of Manion et.al<9>on trans-1,2-CHClCHCl hydrogenolysis with those obtained in the Ar system. In this system Manion reports the starting ratio of trans/cis-CHClCHCl was 0.03. The overall equilibrium occurred with a ratio of trans/cis-CHClCHCl of 1.46 at around 650°C. Both isomer started slowly to convert CH_2CHCl and C_2H_4 with decrease in the ratio level of trans/cis-CHClCHCl. We report isomerization decay of pure trans isomer in our DCEE/O_2 system started at 575° C. The ratio of trans/cis-CHClCHCl was 2.03 at 600°C. Both isomer rapidly reacts with

oxy radial (O, O_2, H_2O) and Cl, the overall decay of both isomer then occurred with increase in CO, CO_2.

4.2.6 Material Balance

The material balance on carbon gives important information about high molecular weight compounds and soot which are not quantitatively detected. The carbon material balances for the present study are listed in Tables 4.4 to 4.9 as shown section 4.6.

The DCEE/CH_4/Ar system indicates poor carbon material balance (83.97% at 825°C, 57.04% 900°C) with increased formation of C_2H_2 (6.05% at 825°C) in addition to benzene at higher temperature all of which are known soot precursors. Formation of high molecular weight species and soot occurred at above 800°C in the absence of O_2. In DCEE/CH_4/O_2 system the carbon material balances is improved. Formation of high molecular weight species and soot formation is observed in fuel rich system, where the material balance drops below 90 % at 850°C.

Stoichiometric and fuel lean systems show good material balances above 90 % and good carbon material balances at high temperature with increasing CO and CO_2. The DCEE/O_2/Ar system also shows good material balance where significant conversion to CO and CO_2 is present. The DCEE/Ar system gives good material balance and data are shown in Table 4.8.

4.3 Effect of Oxygen

The DCEE/CH_4/O_2/Ar system with 2% O_2 is still fuel rich. The 2% O_2 shows slightly slower decay CHClCHCl than for 6% and 4% O_2. 4% and 6% cases O2 show no difference in decomposition of CHClCHCl. The CHClCHCl decreases a slightly faster in fuel lean than under stoichiometric and fuel rich conditions.

Methane, when present under fuel rich conditions, decreases much slower than under oxidative conditions as shown Figures 4.19 to 4.22, which plot its decay vs time

and temperature, in the three reaction environments. Methane in fuel rich system did not completely decay at 850°C, however it was 100% converted in the fuel lean system at 800°C. A trend of increasing rate of decomposition is observed from fuel rich to stoichiometric and then to fuel lean. This results found in both decomposition of CHClCHCl and methane as a function of reaction time, as is illustrated in Figures 4.9 to 4.14.

The effect of oxygen is further shown in Figures 4.25 to 4.40 which illustrate the product distribution vs temperature and reaction time in fuel rich, stoichiometric and fuel lean systems. The decay of HCCCl is observed to start at 750°C for fuel rich and at 770° C for stoichiometric and fuel lean conditons. The conversion of CO into CO_2 was observed at 775°C for 4% and 6% CH_4/O_2 systems but not seen in these temperature range for 2% O_2.

Relative concentration of C_2H_2, C_2H_4, C_6H_6, CH_2CHCl, CH_3Cl, are observed to increased under fuel rich conditions and decreases in fuel lean. CH_2CCl_2 is unique, however, it decreases under both fuel rich and fuel lean conditions. In the fuel rich system higher 18 % C_2H_2 is observed at high temperature 825°C. 6 % in pyrolysis with CH_4 at the same temperature and 6.2 % in the stoichiometric at 775°C, 4 % in the fuel lean at the 750°C, at all 1.0 second reaction time. This indicates that the fuel rich system in Ar produces the same pyrolysis reaction environment from the parent compound and intermediate products as the pyrolysis system with methane.

4.4 Comparison between Decay of trans-and cis-1,2-CHClCHCl

Experiments starting with only one isomer show similar product distribution for trans and cis isomers, at 725°C in the DCEE/CH_4/O_2(6%)/Ar system as shown Figures 4.54 to 4.57. Decay of the specific trans and cis isomer is, however, different. Decay of cis DCEE is very faster than decay of trans DCEE. The concentration of products from the cis isomer, especially CO, is also observed to be higher than those from the trans isomer.

The cis isomer seems to have a higher dissociation rate constant at this system. Comparison of the product distribution and decay, with the conversion (C/Co) at 725°C and 1.0 residence time in the DCE/CH_4/O_2(6%)/Ar system, shows the following :

Table 4.2 Comparison of the Decay between trans - and cis - CHClCHCl

Species (Reactants)	trans - CHClCHCl	cis - CHClCHCl
CH_4	0.736	0.715
CHClCHCl (Both isomers)	0.725	0.422
CO	0.333	0.578
CO_2	0.027	0.034
C_2H_2	0.031	0.045
C_2H_4	0.029	0.032
CH_3Cl	0.013	0.026
HCCCl	0.020	0.025
CH_2CHCl	0.039	0.062
CH_2CCl_2	0.013	0.008
C_6H_6	0.006	0.006

The same difference is observed at 725°C in DCEE/CH_4/Ar system as shown Figures 4.48 and 4.59. Cis isomer decomposes faster than trans isomer at 1.0 residence time. CH_2CCl_2 from the cis isomer is produced slightly faster than from the trans isomer. Comparison of the product distribution and decay in the DCEE/CH_4/Ar system, shows the following:

Table 4.3 Comparison of the Decay between trans - and cis - CHClCHCl

Species (Reactants)	trans - CHClCHCl	cis - CHClCHCl
CH_4	0.923	0.940
CHClCHCl (Both isomers)	0.941	0.860
HCCCl	0.012	0.012
CH_2CHCl	0.001	0.002
CH_2CCl_2	0.020	0.024

4.5 Modeling in CHClCHCl/Ar Pyrolysis

An initial reaction mechanism for CHClCHCl/Ar system is developed. The unimolecular dissociation reactions of CHClCHCl are the most important reaction in this reaction system under initiation conditions. Quantum Kassel calculations are used to account for fall off. Figures 4.1 and 4.2 shows that the HCl elimination reaction channel is favored over Cl loss channel. The input data to the QRRK calculations are shown in Table 4.10.

	A (1/s)	Ea (Kcal/mol)
$CHClCHCl \rightarrow HCCCl + HCl$	3.53E15	89.55
$CHClCHCl \rightarrow CHCHCl + Cl$	1.05E14	69.68

The major intermediate product from the destruction of 1,2-CHClCHCl, HCCCl, is relatively stable, as compared to other chloroethane products. HCCCl is formed from the dissociation of CHClCHCl :

$CHClCHCl \rightarrow HCCCl + HCl$

But this pathway will compete with Cl bond cleavage at increasing temperature. The formation of Cl atoms in initial destruction step gives to a strong acceleration of CHClCHCl consumption via chain propagation reactions.

$CHClCHCl \rightarrow CHCHCl + Cl$

$CHClCHCl + Cl \rightarrow CHClCCl + HCl$

$CHCHCl = C_2H_2 + Cl$

CHClCCl radical leads to high concentration of HCCCl via beta scission

$CHClCCl \rightarrow HCCCl + Cl$

Hydrogen chloride is formed primarily from the unimolecular decomposition (HCl elimination) of CHClCHCl. HCl will combine with parent compound CHClCHCl to form chemically activated adduct $[CH_2ClCHCl_2]^*$, which reacts to products as follows:

$CHClCHCl + HCl \leftrightarrow [CH_2ClCHCl_2]^*$

$\rightarrow CH_2Cl + CHCl_2$ $\quad \Delta H_{rxn} = 87.30$ Kcal/mole

$\rightarrow CHCl_2CH2 + Cl$ $\quad \Delta H_{rxn} = 79.64$ Kcal/mole

$\rightarrow$ CH2ClCHCl + Cl $\quad\quad$ ΔH_{rxn} = 75.07 Kcal/mole

$\rightarrow$ CH_2CCl_2 + HCl $\quad\quad$ ΔH_{rxn} = 13.25 Kcal/mole

$\rightarrow$ $CH_2ClCHCl_2$ $\quad\quad$ ΔH_{rxn} = -13.38 Kcal/mole

The Quantum Kassel calculations for temperature 500°C to 1000°C and pressure of 0.1 to 10 atm indicate that the CH_2CCl_2 + HCl channel slightly favored at low temperature as shown in Figures 4.5 and 4.6. This molecular addition reaction across a double bond is a major channel in the formation of CH_2CCl_2. The combination reaction, HCl + HCCCl, is only a minor channel in formation of 1,1-DCEE.

HCCCl + HCl = CH_2CCl + Cl

HCCCl + HCl = CHCHCl + Cl

Quantum Kassel results show CH2CCl + Cl channel is favored over CHCHCl + Cl channel in Figure 4.7 to 4.8

The major reaction responsible for the decay of CH_2CCl_2 is

CH_2CCl_2 + Cl $\rightarrow$ CCl_2CH + HCl

The unimolecular dissociation reaction of CH_2CCl_2 becomes more important with increasing temperature.

$CH_2CCl_2 \rightarrow$ HCCCl + HCl

CH_2CCl_2 will decompose or react further as follow reaction:

$CH_2CCl_2 \rightarrow CH_2CCl$ + Cl

$CH_2CCl \rightarrow$ HCCCl + H

$CCl_2CH \rightarrow$ HCCCl + Cl

CH_2CCl_2 + HCl $\rightarrow$ CH_3CCl_3

A small mechanism of elementary reaction.is listed in Table 4.15 together with the rate parameters and corresponding sources. This kinetic mechanism consists of 92 elementary reactions with 48 species. Experimental data are compared with model prediction in Figures 4.60 to 4.65 for reagent decomposition and product distribution between 675°C and 725°C. The comparison of CHClCHCl, HCCCl in Figure 4.60 and is

shown as function of temperature at 1.0 second residence time and function of reaction time from 650°C to 725°C. Prediction for loss for of the 1,2-DCEE and CH_4 and product distribution match well, although decay of CHClCHCl slightly faster in the model at 725°C. The model predictions of CHClCHCl, HCCCl show good agreement at 700°C as shown Figure 4.60. The minor products such as C_2H_2, CH_2CHCl, CH_2CCl_2, C_2Cl_2, C_2HCl_3, CH_2ClCCl_3, $CHCl_2CHCl_2$ is compared with model prediction in Figure 4.62 and 4.63 at 700°C, and agreement of model with experiment is reasonable for an initial model.

4.6 Figures and Tables Showing Experimental Data

This section includes Figures and Tables for QRRK Analysis and Experimental Data.

Table 4.4 Material Balance for 100 Moles Carbon in $CHClCHCl:CH_4:O_2:Ar = 1:1:2:96$

	Temperature (°C)					
Species	725	750	775	800	825	850
CH_4	31.51	26.77	23.43	19.96	15.13	12.89
C_2H_2	0.05	1.80	3.73	8.79	17.93	10.39
C_2H_4	0.11	1.27	2.33	3.80	3.79	2.44
C_2H_6	0.03	0.02	0.13	-	0.07	0.01
CH_3Cl	0.04	0.20	0.71	1.22	0.89	0.40
C_3H_4	0.37	0.54	0.29	-	-	-
HCCCl	1.12	2.21	2.87	2.65	0.68	0.16
CH_2CHCl	0.57	1.69	3.57	4.43	1.85	0.15
CH_2Cl_2	0.07	0.21	0.53	0.59	0.18	-
C_2Cl_2	0.35	0.61	0.66	0.30	0.11	-
CH_2CCl_2	1.67	1.29	0.59	0.30	-	-
CHClCHCl	61.64	50.27	35.13	14.13	2.25	0.22
CH_3CCl_3	0.07	0.06	0.05	0.03	0.01	-
C_6H_6	0.65	1.42	2.46	2.50	1.30	0.62
$C_6H_6CH_3$	0.02	0.09	0.11	0.05	-	-
C_6H_5Cl	0.17	0.22	0.31	0.62	0.56	0.18
CO	1.11	5.20	13.01	31.19	49.03	54.65
CO_2	0.20	0.47	1.06	1.75	3.85	5.38
Total (%)	99.75	94.34	90.97	92.31	97.63	87.49

(Residence Time : 1.0 sec.)

Table 4.5 Material Balance for 100 Moles Carbon in $CHClCHCl:CH_4:O_2:Ar = 1:1:4:94$

	Temperature (°C)				
Species	700	725	750	775	800
CH_4	30.60	28.17	25.70	17.00	-
C_2H_2	-	0.59	2.62	6.20	-
C_2H_4	0.07	0.12	2.02	3.63	-
C_2H_6	0.03	0.02	0.02	0.02	-
CH_3Cl	0.02	0.18	0.58	1.06	-
C_3H_4	0.18	0.30	0.31	-	-
HCCCl	0.68	1.29	2.20	1.52	-
CH_2CHCl	0.41	1.54	3.15	4.85	-
CH_2Cl_2	0.05	0.13	0.33	0.20	-
C_2Cl_2	0.27	0.60	0.79	0.14	-
CH_2CCl_2	1.73	1.28	0.75	-	-
CHClCHCl	59.91	51.13	43.00	8.71	0.41
CH_3CCl_3	0.08	0.09	0.07	0.02	-
C_6H_6	0.46	1.03	0.62	1.11	-
$C_6H_6CH_3$	0.02	0.06	0.12	-	-
C_6H_5Cl	0.16	0.13	0.27	0.35	-
CO	-	9.96	11.30	41.97	2.04
CO_2	-	0.80	0.71	3.08	90.80
Total (%)	94.67	97.42	94.56	89.86	93.25

(Residence Time : 1.0 sec.)

Table 4.6 Material Balance for 100 Moles Carbon in $CHClCHCl:O_2:Ar = 1:4:95$

	Temperature (°C)				
Species	575	600	625	650	675
C_2H_2	0.07	0.55	1.66	2.72	2.76
HCCCl	0.53	0.77	0.49	-	-
CH_2CHCl	0.46	1.48	1.49	-	-
CH_2Cl_2	-	0.12	0.14	0.05	-
CH_2CCl_2	-	0.08	0.22	0.29	0.10
CHClCHCl	95.06	59.93	22.51	3.95	0.61
C_2HCl_3	-	0.55	1.33	1.07	0.33
CO	6.18	28.09	59.73	69.57	71.73
CO_2	1.09	1.99	5.58	9.34	16.12
Total (%)	103.39	93.56	93.15	86.99	91.65

(Residence Time : 1.0 sec.)

Table 4.7 Material Balance for 100 Moles Carbon in CHClCHCl:CH_4:Ar = 1:1:98

	Temperature (°C)								
Species	725	750	775	800	825	850	900	950	1000
CH_4	30.91	30.37	31.36	29.26	23.16	21.65	16.69	15.32	14.47
C_2H_2	-	-	0.25	1.15	6.05	5.91	19.89	21.33	14.92
C_2H_4	-	0.05	0.09	0.18	0.39	0.82	0.97	1.16	0.75
CH_3Cl	-	-	-	-	0.01	0.02	0.01	-	-
C_3H_4	-	0.80	1.31	1.71	1.14	-	-	0.19	0.14
HCCCl	0.82	2.14	3.93	5.93	7.38	8.49	6.39	0.51	0.29
CH_2CHCl	0.09	0.24	0.52	0.97	1.23	1.24	0.27	-	-
CH_2Cl_2	0.02	0.06	0.13	0.23	0.53	0.37	0.19	0.07	0.02
C_2Cl_2	0.11	0.26	0.30	0.33	0.49	0.20	0.14	-	-
CH_2CCl_2	1.30	1.59	1.33	0.93	0.93	0.23	-	-	-
CHClCHCl	63.07	61.48	52.82	46.61	38.33	20.96	6.84	1.15	0.43
CH_3CCl_3	0.03	0.03	0.02	0.02	0.03	0.03	0.02	-	-
C_6H_6	-	0.17	1.02	2.04	3.42	5.34	4.94	6.10	3.16
$C_6H_6CH_3$	-	-	-	0.14	0.14	0.33	0.09	0.07	0.07
C_6H_6Cl	-	-	-	0.16	0.74	0.42	0.60	0.56	0.22
Total (%)	96.35	97.19	93.08	89.66	83.97	66.01	57.04	46.46	34.47

(Residence Time : 1.0 sec.)

Table 4.8 Material Balance for 100 Moles Carbon in CHClCHCl:Ar = 1:99

	Temperature (°C)			
Species	650	675	700	725
CH_4	0.03	0.04	0.03	-
C_2H_2	0.02	0.09	0.19	0.34
HCCCl	1.49	3.26	13.93	28.05
CH_2CHCl	0.44	0.41	0.39	0.30
C_2Cl_2	-	-	0.03	0.17
CH_2CCl_2	0.07	0.08	0.04	0.07
CHClCHCl	95.31	91.24	81.02	66.49
CH_3CCl_3	-	-	0.03	0.08
C_2HCl_3	-	-	0.04	0.09
C_6H_6	-	-	0.06	-
CH_2ClCCl_3	-	-	0.08	0.16
$CHCl_2CHCl_2$	-	-	0.04	0.08
C_2Cl_4	-	0.04	0.04	0.06
Total (%)	97.36	95.16	95.92	95.89

(Residence Time : 1.0 sec.)

Table 4.9 Material Balance for 100 Moles Carbon in CHClCHCl:CH_4:O_2:Ar = 1:1:6:92

	Temperature (°C)				
Species	700	725	750	775	800
CH_4	30.41	24.53	21.81	7.81	0.01
C_2H_2	0.07	2.09	4.08	3.51	-
C_2H_4	0.19	1.91	3.09	1.17	-
C_2H_6	0.03	0.03	0.01	-	-
CH_3Cl	0.10	0.44	1.10	0.12	-
C_3H_4	0.20	0.20	-	-	-
HCCCl	0.86	1.51	2.01	0.12	-
CH_2CHCl	0.95	2.59	5.16	0.41	-
CH_2Cl_2	0.09	0.20	0.31	-	-
C_2Cl_2	0.43	0.69	0.42	-	-
CH_2CCl_2	1.68	0.85	0.04	-	-
CHClCHCl	56.12	48.36	25.95	0.25	0.23
CH_3CCl_3	0.11	0.07	0.03	-	-
C_6H_6	0.70	1.18	1.30	1.20	-
$C_6H_6CH_3$	0.06	0.12	0.12	-	-
C_6H_5Cl	0.18	0.22	0.30	0.02	-
CO	2.52	11.10	28.84	69.80	1.69
CO_2	0.27	0.89	1.30	8.51	91.66
Total (%)	94.97	96.98	95.87	92.92	93.59

(Residence Time : 1.0 sec.)

Table 4.10 DISSOC Input Parameter

$CHClCHCl \rightarrow$ Products			
Reaction	A	n	Ea
k_1 $CHClCHCl \rightarrow HCCCl + HCl$	1.05E14	0.00	69.68
k_2 $CHClCHCl \rightarrow CHCHCl + Cl$	3.53E15	0.00	89.55

A's in sec^{-1} and cm^3/mole-sec, Ea in Kcal/mole

$\langle v \rangle = 909.3\ cm^{-1}$, Evaluated from computer code CPFIT.

$\sigma = 5.05$ Å, $e/k = 418.57$ K, LJ parameter from The Properties of Gases and Liquids, 3rd Ed., Reid, R.C., J.M. Prausnitz, and T.K. Sherwood.

k_1 : Transition State Theory : loss of no rotor, $\Delta S^{\neq} = 0.0$, and degeneracy of 2.
$A_1 = 10^{13.72} \times 2$, $E_a = \Delta H + 37.5$ (this study).

k_2 : A_2 from A_{-2} Microscopic Reversibility, Ea = ΔH-RT. Chiang, H.M. and J.W. Bozzelli, "Formation of Chlorinated Ethylene Intermediates in Pyrolysis of CH_2Cl_2 and CH_2Cl_2/CH_4" submitted to 25th Symposium (International) on Combustion/The Combustion Institute, 1994, Irvine, CA.. ($A_{-2} = 5.00E13$, Ea = 0.0).

Table 4.11 DISSOC Input Parameter

$CH_2CCl_2 \rightarrow$ Products			
Reaction	A	n	Ea
k_1 $CH_2CCl_2 \rightarrow HCCCl + HCl$	1.05E14	0.00	69.81
k_2 $CH_2CCl_2 \rightarrow CH_2CCl + Cl$	4.47E15	0.00	89.76

A's in sec^{-1} and cm^3/mole-sec, Ea in Kcal/mole

$\langle v \rangle = 909.3\ cm^{-1}$, Evaluated from computer code CPFIT.

$\sigma = 5.01$ Å, $e/k = 399.43$ K, LJ parameter from The Properties of Gases and Liquids, 3rd Ed., Reid, R.C., Prausnitz, J.M., and Sherwood, T.K.

k_1 : Transition State Theory : loss of no rotor, $\Delta S^{\neq} = 0.0$, and degeneracy of 2.
$A_1 = 10^{13.72} \times 2$, $E_a = \Delta H + 37.5$ (this study).

k_2 : A_2 from A_{-2} Microscopic Reversibility, Ea = ΔH-RT.
$A_{-2} = 5.00E13$, Ea = 0.0, Ref : Table 4.10.

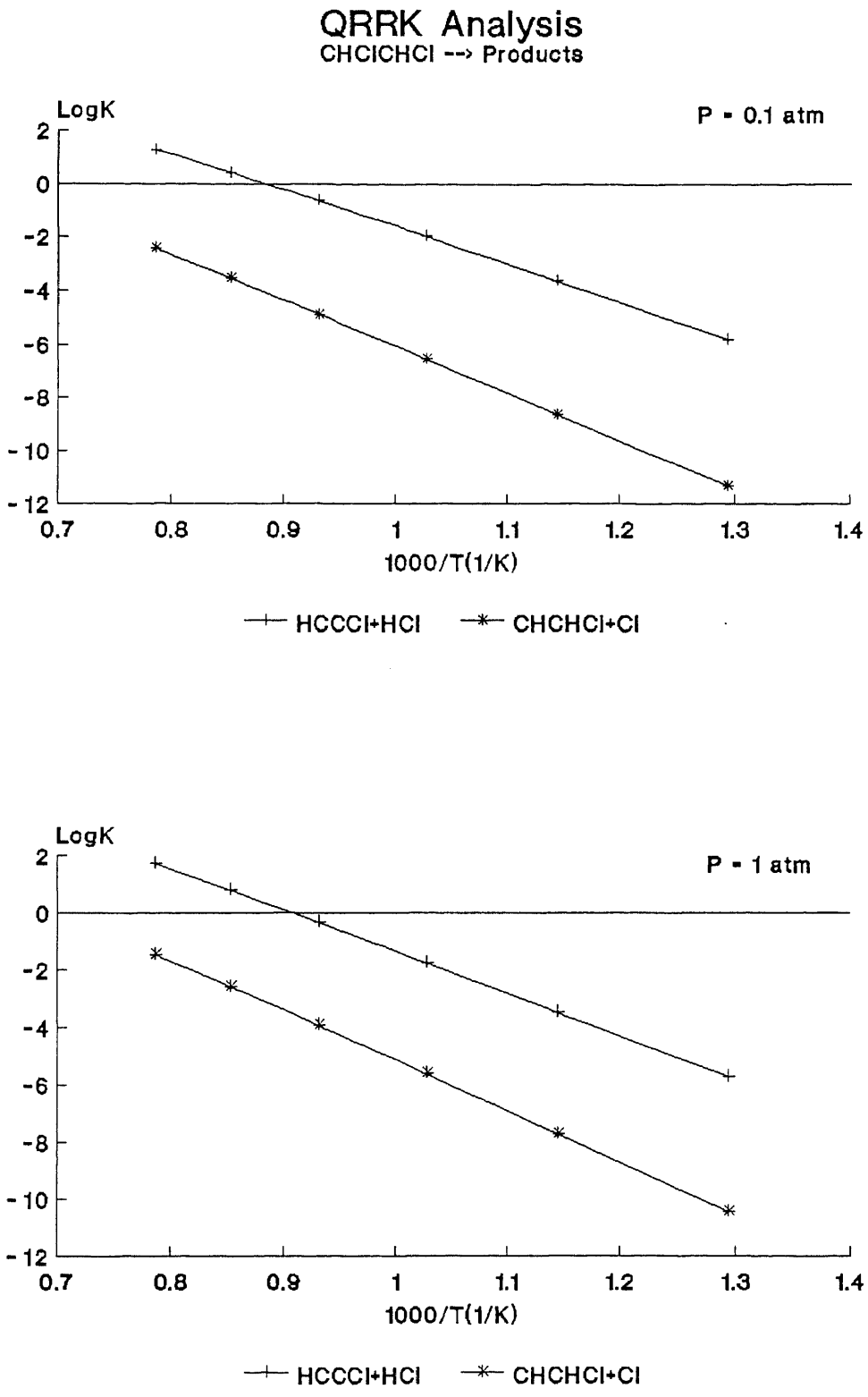
QRRK Analysis
CHClCHCl --> Products
LogK
P = 0.1 atm
2
0
-2
-4
-6
-8
-10
-12
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
HCCCl+HCl
CHCHCl+Cl
LogK
P = 1 atm
2
0
-2
-4
-6
-8
-10
-12
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
HCCCl+HCl
CHCHCl+Cl

Figure 4.1

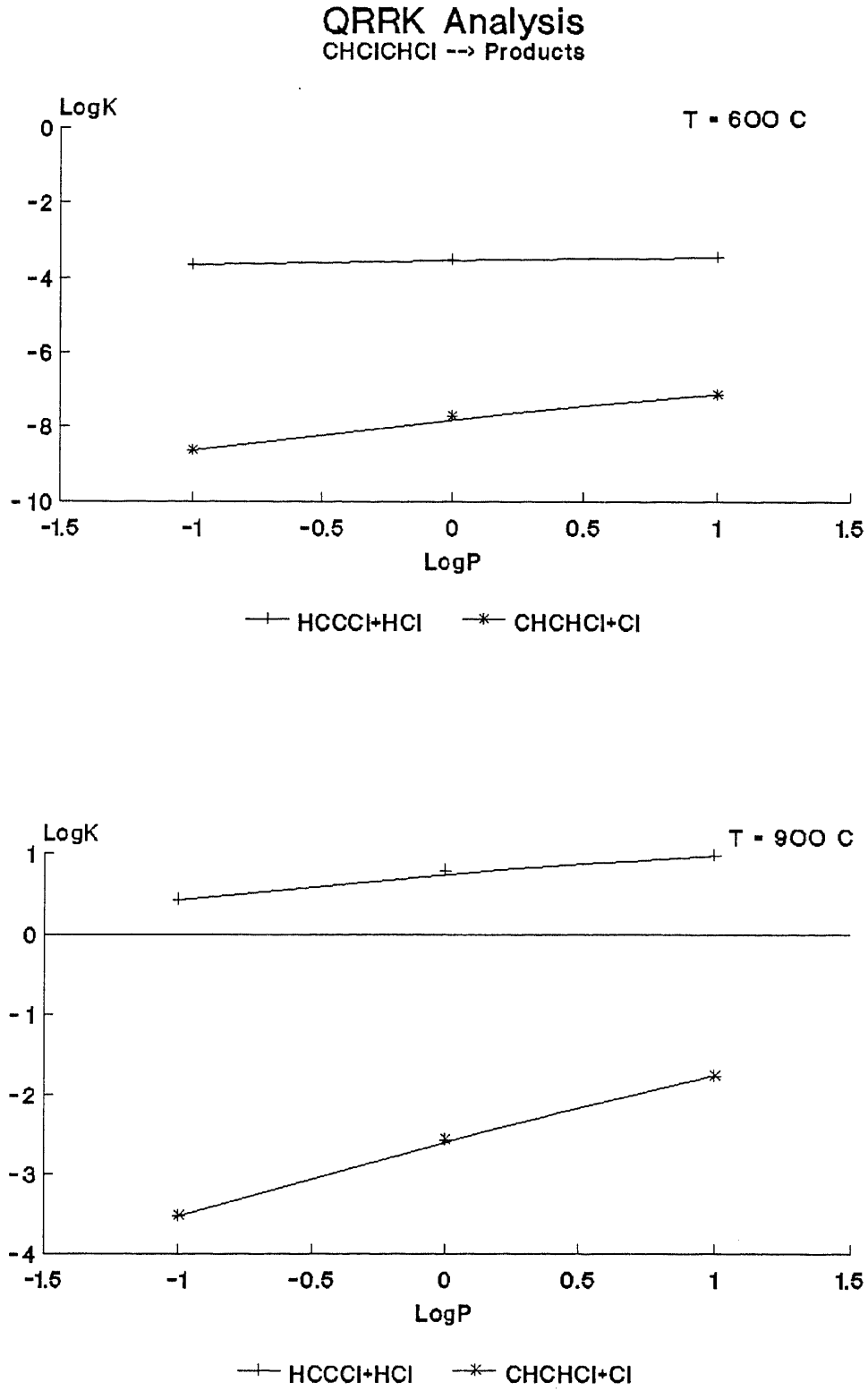
QRRK Analysis
CHClCHCl --> Products
LogK
T = 600 C
0
-2
-4
-6
-8
-10
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
HCCCl+HCl
CHCHCl+Cl
LogK
T = 900 C
1
0
-1
-2
-3
-4
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
HCCCl+HCl
CHCHCl+Cl

Figure 4.2

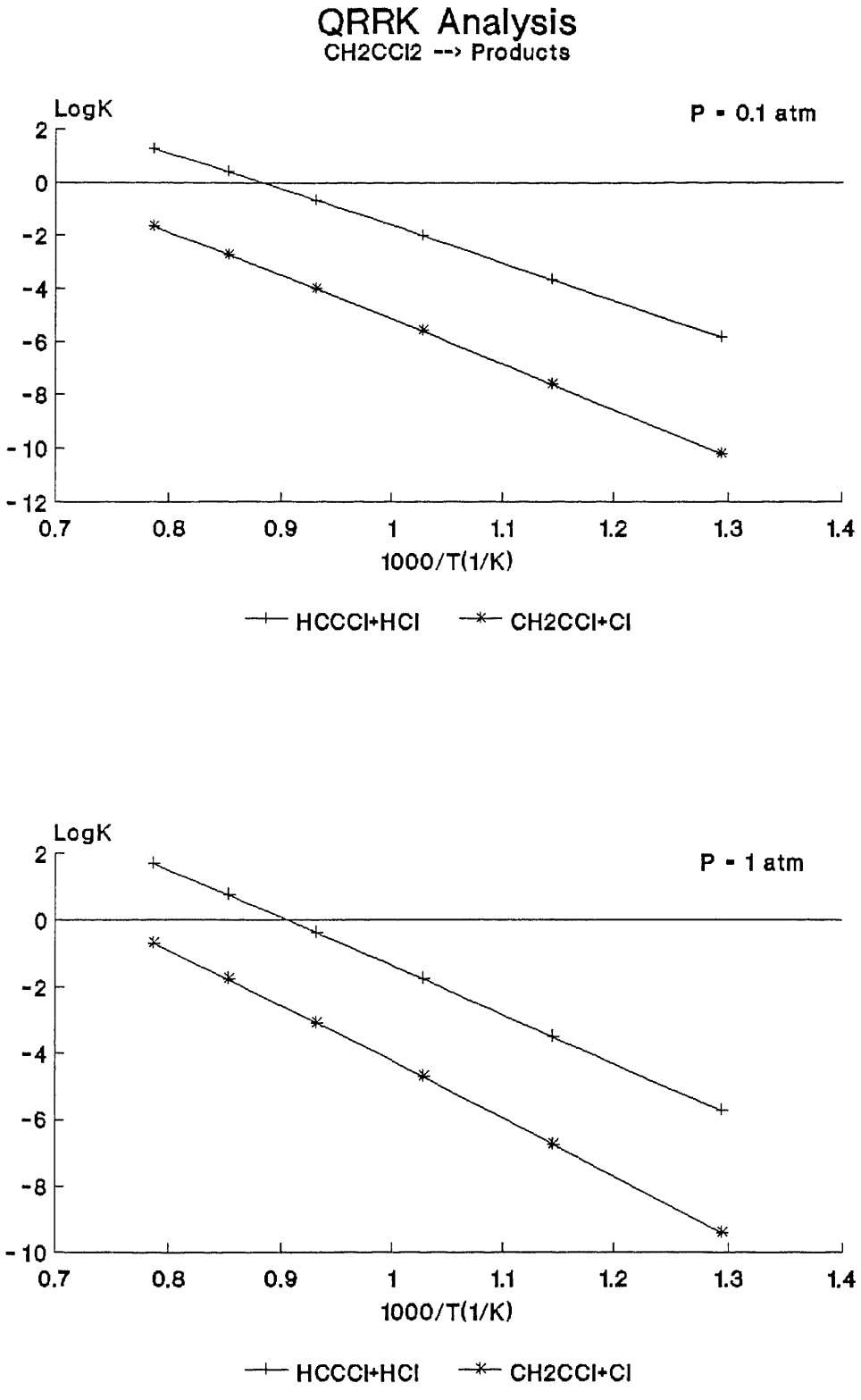
QRRK Analysis
CH2CCl2 --> Products
LogK
P = 0.1 atm
2
0
-2
-4
-6
-8
-10
-12
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
HCCCl+HCl
CH2CCl+Cl
LogK
P = 1 atm
2
0
-2
-4
-6
-8
-10
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
HCCCl+HCl
CH2CCl+Cl

Figure 4.3

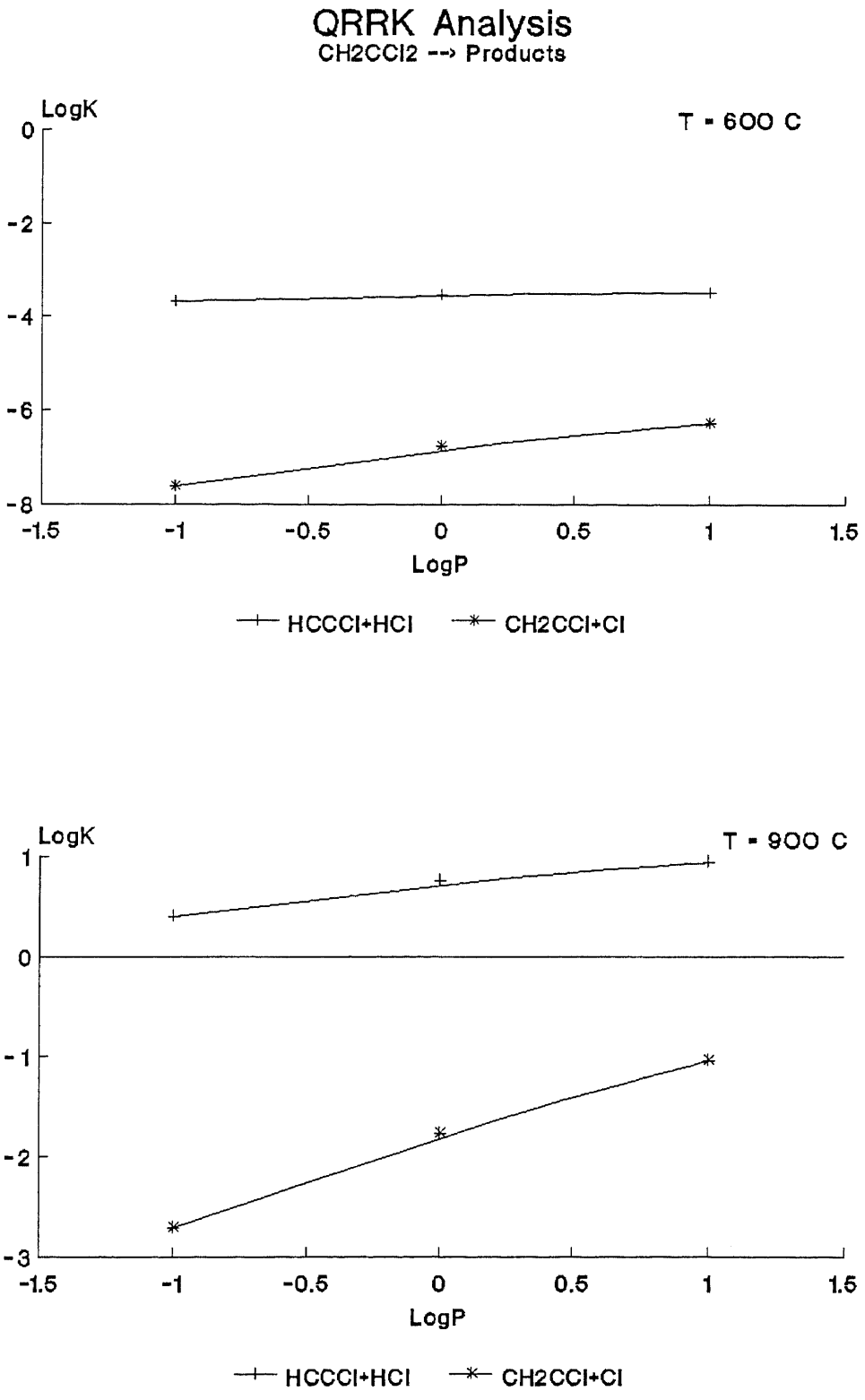
QRRK Analysis
CH2CCl2 --> Products
LogK
T = 600 C
0
-2
-4
-6
-8
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
HCCCl+HCl
CH2CCl+Cl
LogK
T = 900 C
1
0
-1
-2
-3
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
HCCCl+HCl
CH2CCl+Cl

Figure 4.4

Table 4.12 CHEMACT Input Parameter

$CHClCHCl + HCl \rightarrow$ Products			
Reaction	A	n	Ea
k_1 $CHClCHCl + HCl \rightarrow CH_2ClCHCl_2$	4.88E11	0.00	41.00
k_{-1} $CH_2ClCHCl_2 \rightarrow CHClCHCl + HCl$	2.44E13	0.00	54.38
k_2 $CH_2ClCHCl_2 \rightarrow CH_2Cl + CHCl_2$	1.06E17	0.00	85.40
k_3 $CH_2ClCHCl_2 \rightarrow CHCl_2CH_2 + Cl$	1.34E16	0.00	77.74
k_4 $CH_2ClCHCl_2 \rightarrow CH_2ClCHCl + Cl$	4.53E15	0.00	73.17
k_5 $CH_2ClCHCl_2 \rightarrow CH_2CCl_2 + HCl$	6.10E12	0.00	54.25

A's in sec^{-1} and cm^3 / mole-sec, Ea in Kcal / mole

$\langle v \rangle$ = 916.44 cm^{-1}, Evaluated from computer code CPFIT.

σ = 5.72 Å, e/k = 498.9 K, LJ parameter from The Properties of Gases and Liquids, 3rd Ed., Reid, R.C., J.M. Prausnitz, and T.K. Sherwood.

k_1 : A_1 from A_{-1} Microscopic Reversibility.

k_{-1} : Transition State Theory : loss of a rotor, $\Delta S^{\neq}$ = -4.3, and degeneracy of 4. $A_{-1} = 10^{13.72} \times 10^{(-4.3/4.6)} \times 4$, $E_a = \Delta H + 41$. Weissman, M., and S.W. Benson, Int. J. Chem. Kinet., Vol.16, 1984 and Dai, H.L., et.al., J. Chem. Phys., 77, (1982) : 4494:

k_2 : A_2 from A_{-2} Microscopic Reversibility, Ea=ΔH-RT. Chiang, H.M. and J.W. Bozzelli, "Formation of Chlorinated Ethylene Intermediates in Pyrolysis of CH_2Cl_2 and CH_2Cl_2/CH_4" submitted to 25th Symposium (International) on Combustion/The Combustion Institute, 1994, Irvine, CA.. (A_{-2} = 9.5E12, Ea = 0.0).

k_3 : A_3 from A_{-3} Microscopic Reversibility, Ea = ΔH - RT. (A_{-3} = 4.30E13, Ea = 0.0, Ref : k_2).

k_4 : A_4 from A_{-4} Microscopic Reversibility, Ea = ΔH - RT. (A_{-4} = 4.15E13, Ea = 0.0, Ref : k_2).

k_5 : Transition State Theory : loss of a rotor, $\Delta S^{\neq}$ = -4.3, and degeneracy of 1. $A_{-1} = 10^{13.72} \times 10^{(-4.3/4.6)} \times 1$, $E_a = \Delta H + 41$. (Ref : k_{-1}).

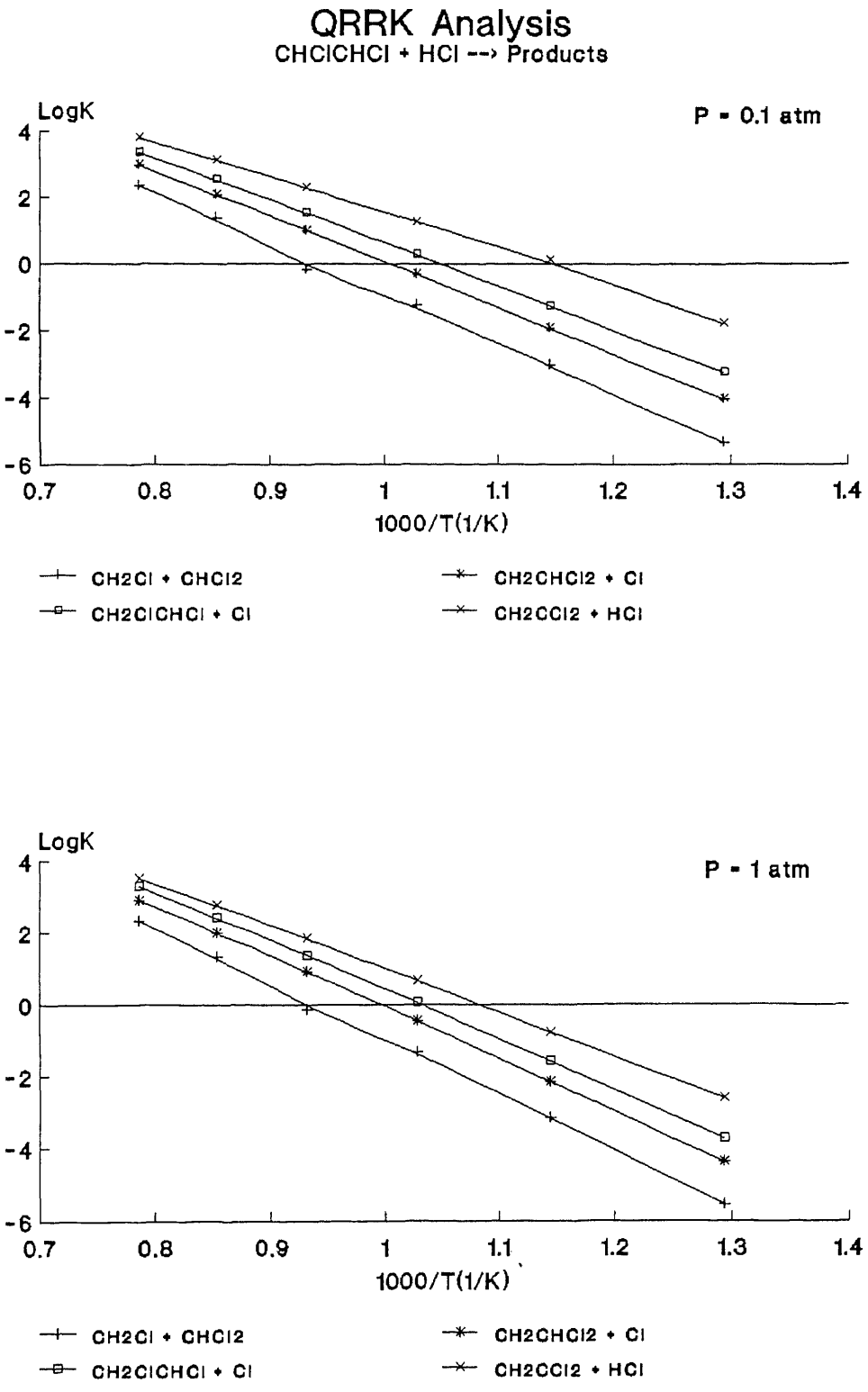
QRRK Analysis
CHClCHCl + HCl --> Products
LogK
P = 0.1 atm
4
2
0
-2
-4
-6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
CH2Cl + CHCl2
CH2ClCHCl + Cl
CH2CHCl2 + Cl
CH2CCl2 + HCl
LogK
P = 1 atm
4
2
0
-2
-4
-6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
CH2Cl + CHCl2
CH2ClCHCl + Cl
CH2CHCl2 + Cl
CH2CCl2 + HCl

Figure 4.5

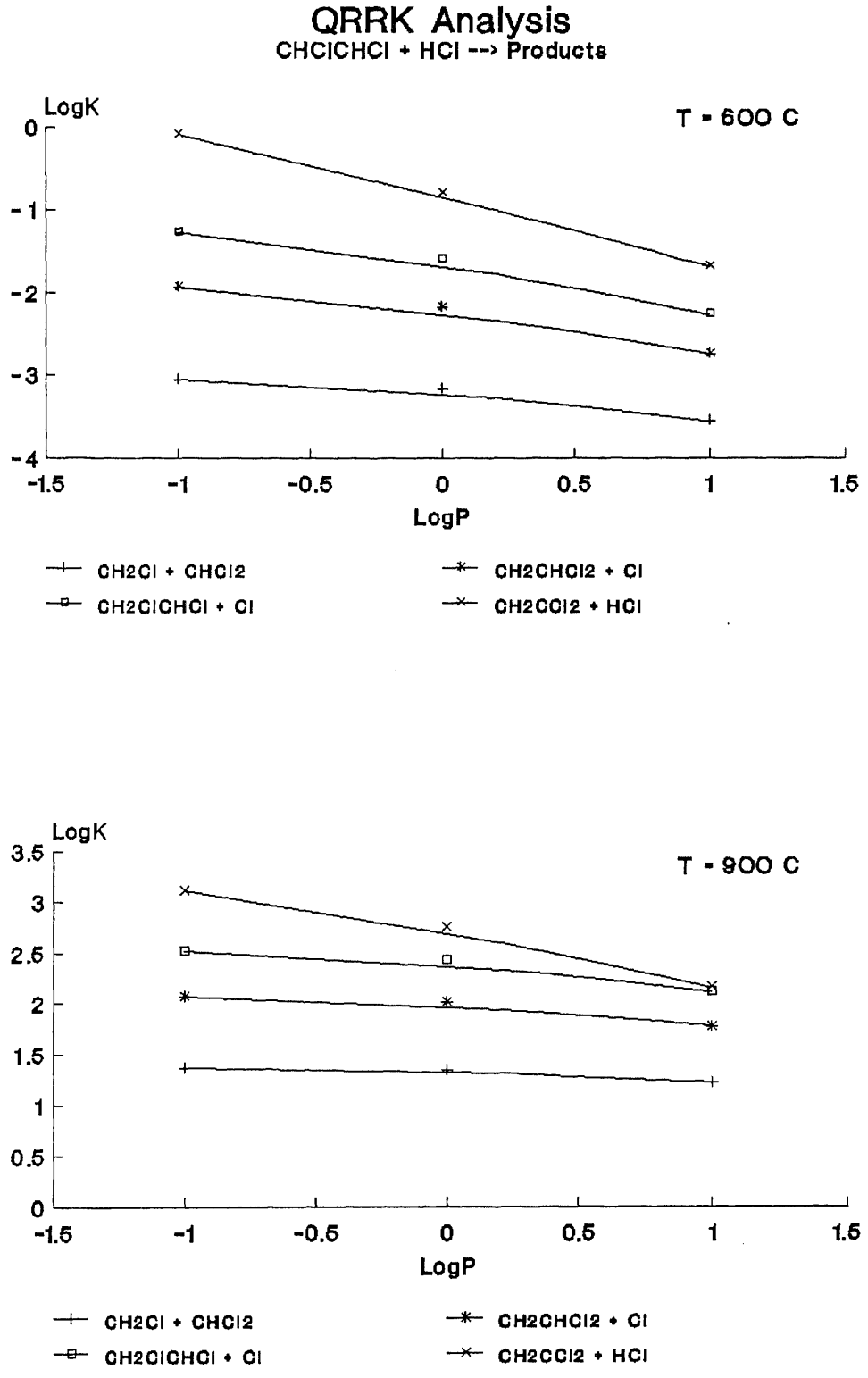
QRRK Analysis
CHClCHCl + HCl --> Products
LogK
T = 600 C
0
-1
-2
-3
-4
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
CH2Cl + CHCl2
CH2ClCHCl + Cl
CH2CHCl2 + Cl
CH2CCl2 + HCl
LogK
T = 900 C
3.5
3
2.5
2
1.5
1
0.5
0
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
CH2Cl + CHCl2
CH2ClCHCl + Cl
CH2CHCl2 + Cl
CH2CCl2 + HCl

Figure 4.6

Table 4.13 CHEMACT Input Parameter

HCCCl + HCl → Products			
Reaction	A	n	Ea
k_1 HCCCl + HCl → CHClCHCl	9.83E11	0.00	37.50
k_{-1} CHClCHCl → HCCCl + HCl	1.05E14	0.00	69.68
k_2 CHClCHCl → CHCHCl + Cl	3.53E15	0.00	89.55

A's in sec^{-1} and cm^3/mole-sec, Ea in Kcal/mole

$\langle v \rangle = 909.3 cm^{-1}$, Evaluated from computer code CPFIT.

$\sigma = 5.05$ Å, e/k = 418.57 K, Ref : Table 4.10.

k_1 : A_1 from A_{-1} Microscopic Reversibility.

k_{-1} : Transition State Theory : loss of no rotor and degeneracy of 2.
$A_{-1} = 10^{13.72} \times 2$, $E_a = \Delta H + 37.5$ (This study).

k_2 : A_2 from A_{-2} Microscopic Reversibility, Ea = ΔH-RT.
A_{-2} = 5.00E13, Ea = 0.0, Ref : Table 4.10

Table 4.14 CHEMACT Input Parameter

HCCCl + HCl → Products			
Reaction	A	n	Ea
k_1 HCCCl + HCl → CH2CCl2	9.83E11	0.00	37.50
k_{-1} CH2CCl2 → HCCCl + HCl	1.05E14	0.00	69.81
k_2 CH2CCl2 → CH2CCl + Cl	4.47E15	0.00	86.76

A's in sec^{-1} and cm^3/mole-sec, Ea in Kcal/mole

$\langle v \rangle = 909.3 cm^{-1}$, Evaluated from computer code CPFIT.

$\sigma = 5.01$ Å, e/k = 399.43 K. Ref : Table 4.11.

k_1 : A_1 from A_{-1} Microscopic Reversibility.

k_{-1} : Transition State Theory : loss of no rotor and degeneracy of 2.
$A_{-1} = 10^{13.72} \times 2$, $E_a = \Delta H + 37.5$ (This study).

k_2 : A_2 from A_{-2} Microscopic Reversibility, Ea = ΔH - RT. Ref : Table 4.11.

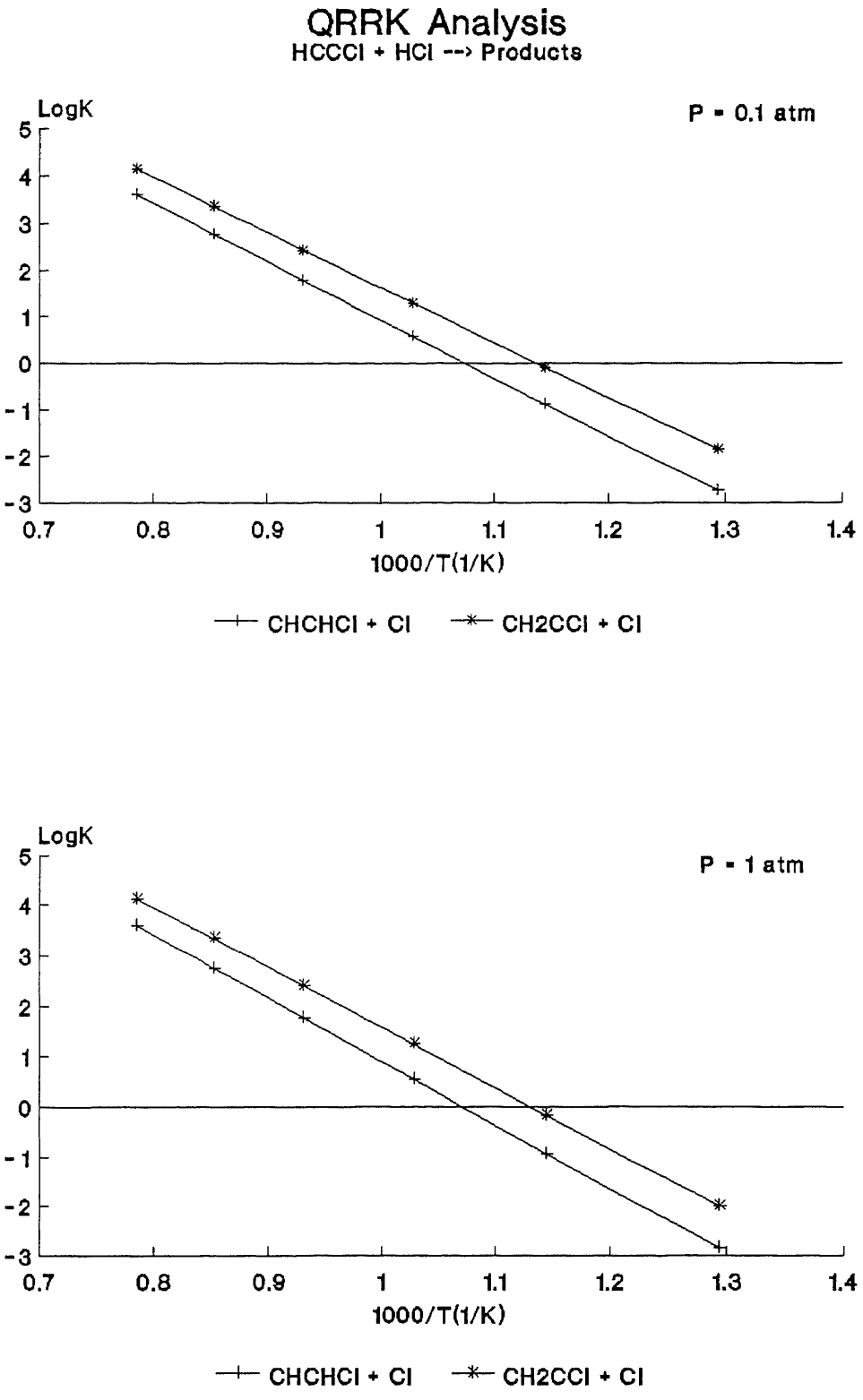
QRRK Analysis
HCCCl + HCl --> Products
LogK
P = 0.1 atm
5
4
3
2
1
0
-1
-2
-3
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
CHCHCl + Cl
CH2CCl + Cl
LogK
P = 1 atm
5
4
3
2
1
0
-1
-2
-3
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1000/T(1/K)
CHCHCl + Cl
CH2CCl + Cl

Figure 4.7

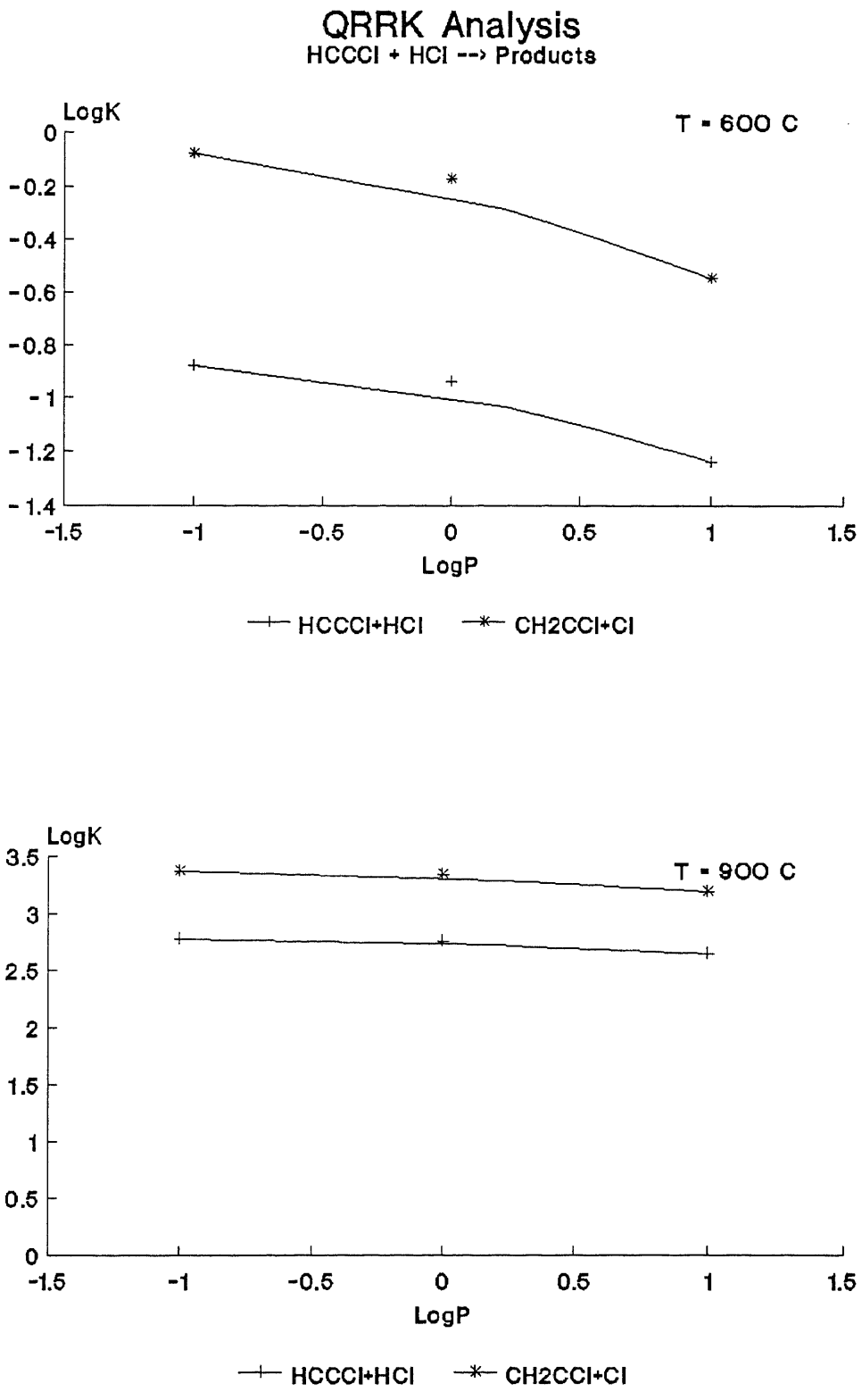
QRRK Analysis
HCCCl + HCl --> Products
LogK
T = 600 C
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
HCCCl+HCl
CH2CCl+Cl
LogK
T = 900 C
3.5
3
2.5
2
1.5
1
0.5
0
-1.5
-1
-0.5
0
0.5
1
1.5
LogP
HCCCl+HCl
CH2CCl+Cl

Figure 4.8

Table 4.15 Mechanism for CHClCHCL/Ar System

REACTION	A	n	Ea	SOURCES
$CHClCHCl = HCCCl + HCl$	1.87E34	-6.14	78.64	DISSOC
$CHClCHCl = CHCHCl + Cl$	2.04E45	-9.55	99.65	DISSOC
$CHClCHCl + Cl = CHClCCl + HCl$	5.00E13	0.00	8.50	1
$CHClCHCl + Cl = CHCHCl + Cl_2$	5.00E13	0.00	33.65	1
$CHClCHCl + HCl = CH_2Cl + CHCl_2$	3.82E48	-9.90	90.35	CHEMACT
$CHClCHCl + HCl = CHCl_2CH_2 + Cl$	1.08E41	-7.80	80.86	CHEMACT
$CHClCHCl + HCl = CH_2ClCHCl + Cl$	6.96E38	-7.19	77.09	CHEMACT
$CHClCHCl + HCl = CH_2CCl_2 + HCl$	1.69E23	-2.97	60.92	CHEMACT
$CHClCHCl + H = CH_2ClCHCl$	7.11E09	0.00	3.42	7
$CHClCHCl + H = C_2H_3Cl + Cl$	2.69E13	0.00	6.67	7
$CHClCHCl + H = CHCHCl + HCl$	1.00E13	0.00	6.50	7
$HCCCl + H = C_2H_2 + Cl$	2.00E13	0.00	7.00	3
$HCCCl + H = C_2H + HCl$	2.00E13	0.00	2.10	4
$HCCCl + Cl = C_2Cl_2 + HCl$	7.50E13	0.00	12.40	5
$HCCCl + HCl = CH_2CCl + Cl$	5.27E24	-3.25	61.31	DISSOC
$HCCCl + HCl = CHCHCl + Cl$	1.73E21	-2.25	62.20	DISSOC
$CHCHCl = C_2H_2 + Cl$	1.30E14	0.00	19.79	6
$CHClCCl = HCCCl + Cl$	2.30E14	0.00	30.50	6
$CHClCCl + Cl = C_2Cl_2 + HCl$	1.77E13	0.00	3.40	2
$CHClCCl + Cl = CHCCl_2 + Cl$	6.66E13	0.00	6.80	2
$CH_2ClCHCl_2 = CH_2ClCHCl + Cl$	5.40E15	0.00	73.27	8
	9.94E40	-7.76	84.96	DISSOC
$CH_2ClCHCl_2 = CHClCHCl + HCl$	2.44E13	0.00	54.38	9
	1.03E21	-2.26	58.23	DISSOC
$CH_2ClCHCl_2 = CH_2CCl_2 + HCl$	6.10E12	0.00	54.25	10
	4.47E16	-1.15	56.23	DISSOC
$CH_2ClCHCl_2 = CHCl_2CH_2 + Cl$	1.55E16	0.00	77.84	11
	2.82E41	-7.59	89.72	DISSOC
$CH_2ClCHCl = C_2H_3Cl + Cl$	6.50E13	0.00	19.84	16
$CHCl_2CH_2 = C_2H_3Cl + Cl$	4.59E14	0.00	22.40	12
$C_2H_3Cl = C_2H_2 + HCl$	1.05E15	0.00	70.41	13
	2.53E27	-4.05	78.18	DISSOC
$C_2H_3Cl = C_2H_3 + Cl$	2.10E15	0.00	92.44	14
	1.51E32	-5.51	98.41	DISSOC
$C_2H_3Cl + Cl = CHCHCl + HCl$	5.00E13	0.00	8.50	1
$C_2H_3Cl + Cl = CH_2CCl + HCl$	2.50E13	0.00	8.50	1
$C_2H_3Cl + H = C_2H_3 + HCl$	1.00E13	0.00	6.50	15
$C_2H_3Cl + H = CH_2ClCH_2$	1.71E09	0.00	0.20	2
$C_2H_3Cl + H = C_2H_4 + Cl$	1.33E13	0.00	5.80	2
$CH_2ClCH_2 = C_2H_4 + Cl$	3.13E13	0.00	19.40	2
$CH_3CCl_3 = CH_2CCl_2 + HCl$	3.35E13	0.00	51.20	16
$CH_3CCl_3 = CH_3CCl_2 + Cl$	4.59E14	0.00	66.60	16
$CH_3CCl_3 = CH_3 + CCl_3$	2.05E14	0.00	77.70	16
$CH_2CCl_2 = HCCCl + HCl$	1.75E34	-6.13	78.73	DISSOC
$CH_2CCl_2 = CH_2CCl + Cl$	1.50E48	-10.30	98.48	DISSOC

Table 4.15 (Continued)

REACTION	A	n	Ea	SOURCES
$CH_2CCl_2 + Cl = CHCCl_2 + HCl$	2.50E13	0.00	8.50	1
$CH_2CCl_2 + H = CH_2CCl + HCl$	1.20E13	0.00	5.50	15
$CH_2CCl_2 + H = CHCl_2CH_2$	7.21E24	-4.89	7.92	16
$CH_2CCl_2 + H = C_2H_3Cl + Cl$	1.00E13	0.00	5.80	16
$CH_2CCl_2 + H = CHCCl_2 + H_2$	1.58E13	0.00	6.00	2
$CH_3CCl_2 = CH_2CCl_2 + H$	2.60E13	0.00	41.40	2
$CH_2CCl = HCCCl + H$	8.24E11	0.00	35.50	18
$CHCCl_2 = HCCCl + Cl$	1.00E10	0.00	14.40	19
$CHCCl_2 + Cl = C_2Cl_2 + HCl$	1.92E13	0.00	3.70	2
$CH_3CHCl_2 = C_2H_3Cl + HCl$	3.66E13	0.00	55.43	20
	2.24E23	-2.90	59.68	DISSOC
$CH_3CHCl_2 = CH_3CHCl + Cl$	1.98E15	0.00	75.71	21
	1.85E44	-8.58	88.07	DISSOC
$CH_3CHCl = C_2H_3Cl + H$	2.21E13	0.00	46.80	2
$CH_2Cl_2 = CHCl + HCl$	6.90E34	-6.54	78.45	7
$CH_2Cl_2 = CH_2Cl + Cl$	5.17E36	-6.87	81.13	7
$C_2HCl_3 = CHCCl_2 + Cl$	1.13E15	0.00	87.30	22
	8.70E39	-7.62	97.82	DISSOC
$C_2HCl_3 = CHClCCl + Cl$	1.58E15	0.00	84.20	22
	1.41E38	-6.97	94.40	DISSOC
$C_2HCl_3 = C_2Cl_2 + HCl$	1.05E14	0.00	74.77	23
	7.88E26	-3.85	80.99	DISSOC
$C_2HCl_3 + Cl = C_2Cl_3 + HCl$	1.70E13	0.00	7.50	1
$C_2HCl_3 + Cl = CHClCCl + Cl_2$	3.00E14	0.00	34.00	1
$C_2HCl_3 + Cl = CHCCl_2 + Cl_2$	3.00E14	0.00	40.20	1
$C_2Cl_4 = C_2Cl_3 + Cl$	1.00E15	0.00	81.50	2
$C_2Cl_3 = C_2Cl_2 + Cl$	1.12E14	0.00	27.98	24
$C_2Cl_2 + Cl = C_2Cl + Cl_2$	1.57E14	0.00	47.00	2
$CHCl_2 + CHCl_2 = CHCl_2CHCl_2$	1.37E47	-11.01	9.68	7
$CHCl_2 + CHCl_2 = CHCl_2CHCl + Cl$	5.10E23	-3.25	9.82	7
$CHCl_2 + CHCl_2 = C_2HCl_3 + HCl$	1.20E30	-5.30	8.69	7
$CH_2ClCCl_3 = C_2HCl_3 + HCl$	3.60E13	0.00	54.25	25
	7.32E21	-2.47	58.48	DISSOC
$CH_2ClCCl_3 = CCl_3CH_2 + Cl$	2.87E15	0.00	79.14	26
	1.28E44	-8.73	91.64	DISSOC
$CH_2ClCCl_3 = CH_2ClCCl_2 + Cl$	1.78E15	0.00	71.35	27
	3.86E38	-7.03	82.19	DISSOC
$CHCl_2CHCl_2 = C_2HCl_3 + HCl$	2.83E13	0.00	54.30	28
	3.04E20	-2.09	57.85	DISSOC
$CHCl_2CHCl_2 = CHCl_2CHCl + Cl$	2.40E15	0.00	74.10	29
	2.87E38	-6.96	84.75	DISSSOC
$CHCl_2CHCl = CHClCHCl + Cl$	4.15E36	-7.76	25.79	2
$CH_4 = CH_3 + H$	7.43E13	0.00	101.00	2
$C_2H_6 = C_2H_5 + H$	3.64E16	0.00	89.50	17
$C_2H_6 = CH_3 + CH_3$	2.03E14	0.00	92.30	17

Table 4.15 (Continued)

REACTION	A	n	Ea	SOURCES
$C_2H_6 = C_2H_4 + H_2$	2.29E17	0.00	67.64	30
$C_2H_6 + Cl = C_2H_5 + HCl$	4.64E13	0.00	0.17	31
$C_2H_5 = C_2H_4 + H$	1.83E39	-7.75	-0.24	7
$C_2H_5 + Cl_2 = C_2H_5Cl + Cl$	7.58E12	0.00	52.82	32
$C_2H_5 + H = CH_3 + CH_3$	5.10E14	0.00	2.85	16
$C_2H_4 = C_2H_3 + H$	2.82E15	0.00	108.00	16
$C_2H_4 + H = C_2H_3 + H_2$	1.50E14	0.00	10.20	33
$C_2H_4 + Cl = C_2H_3 + HCl$	2.39E13	0.00	2.60	34
$C_2H_3 = C_2H_2 + H$	6.24E29	-5.29	46.50	7
$C_2H_3 + H = C_2H_2 + H_2$	9.64E13	0.00	0.00	35
$C_2H_2 = C_2H + H$	1.16E13	0.00	124.00	16
$C_2H_2 + Cl = C_2H + HCl$	1.58E14	0.00	26.90	34
$C_2H + H_2 = C_2H_2 + H$	3.50E12	0.00	2.10	36
$C_2H + C_2H_4 = C_2H_2 + C_2H_3$	1.20E13	0.00	0.00	7
$H + Cl + M = HCl + M$	1.00E17	0.00	0.00	37
$H + HCl = H_2 + Cl$	2.30E13	0.00	3.50	38
$H + Cl_2 = HCl + Cl$	8.59E13	0.00	1.17	39
$Cl + Cl + M = Cl_2 + M$	2.34E14	0.00	-1.80	38

Unit of A factor is cc/(mol sec.) for bimolecular reaction and 1/sec. for unimolecular reactions.
Unit of Ea is Kcal/mol, Temperature range : 675°C - 725°C
DISSOC : apparent rate contant by DISSOC computer code.
CHEMACT : apparent rate contant by CHEMACT computer code.

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4. A taken as that for $C_2H_3Cl + H$, Ea = Ea ($C_2H_3Cl + H$) - 1, Ref : 30.

5. A taken as 1/2 of $C_2H_2 + Cl$, Ea = ΔH + 0.5, Ref : 30.

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   A_{-1} taken as that for $C_2H_2 + Cl$ (A_{-1} = 1.39E14), Ref : 30.

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8. A factor based on Thermodynamics and Microscopic reversibility.
   Ea = ΔH - RT, (A_{-1} = 4.15E13, Ea = 0.0), Ref : 7

Table 4.15 (Continued)

9. A factor based on Transition State Theory. $A = 10^{13.72} \times 10^{(-4.3/4.6)} \times 4$ loss of 1 rotor and $\Delta S^{\neq} = -4.3$, $Ea = \Delta H + 41$, Ref : 34.

10. A factor based on Transition State Theory. $A = 10^{13.72} \times 10^{(-4.3/4.6)} \times 1$ loss of 1 rotor and $\Delta S^{\neq} = -4.3$, $Ea = \Delta H + 41$, Ref : 34.

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18. A factor based on Thermodynamics and Microscopic reversibility. $Ea = \Delta H + 2.0$, A_{-1} taken as the of $C_2H_2 + H$ ($A_{-1} = 1.0E14$), Ref : 17.

19. A factor based on thermodynamics and Microscopic reversibility. $Ea = \Delta H + 2.0$, A_{-1} taken as that of $C_2H_2 + Cl$ ($A_{-1} = 2.0E13$), Ref : 30.

20. A factor based on Transition State Theory. $A = 10^{13.72} \times 10^{(-4.3/4.6)} \times 6$. loss of 1 rotor and $\Delta S^{\neq} = -4.3$, $Ea = \Delta H + 41$, Ref : 34.

21. A factor based on Thermodynamics and Microscopic reversibility. $Ea = \Delta H - RT$, A_{-1} taken as that of CC.C + C. ($A_{-1} = 1.58E13$), Ref : 17.

22. A factor based on Thermodynamics and Microscopic reversibility. $Ea = \Delta H - RT$, A_{-1} taken as that of $C_4H_7 + CH_3$ ($A_{-1} = 2.5E13$), Ref : 17.

23. A factor based on Transition State Theory. $A = 10^{13.72} \times 2$, $Ea = \Delta H + 45$. loss of no rotor and $\Delta S^{\neq} = 0.0$, Ref : 13.

Table 4.15 (Continued)

24. A factor based on Thermodynamics and Microscopic reversibility.
Ea = ΔH + 2.0, A_{-1} taken as that of C≡C + Cl (A_{-1} = 2.0E13), Ref : 30.

25. A factor based on Transition State Theory. $A = 10^{13.72} \times 10^{(-4.3/4.6)} \times 6$.
loss of 1 rotor and $\Delta S^{\neq}$ = - 4.3, Ea = ΔH + 41, Ref : 34.

26. A factor based on Thermodynamics and Microscopic reversibility.
Ea = ΔH - RT, (A_{-1} = 1.9E13, Ea = 0.0), Ref : 7.

27. A factor based on Thermodynamics and Microscopic reversibility.
Ea = ΔH - RT, (A_{-1} = 1.9E13, Ea = 0.0, Ref : 7.

28. A factor based on Transition State Theory. $A = 10^{13.72} \times 10^{(-4.3/4.6)} \times 4$.
loss of 1 rotor and $\Delta S^{\neq}$ = - 4.3, Ea = ΔH + 41, Ref : 34.

29. A factor based on Thermodynamics and Microreversibility,
Ea = ΔH - RT, A_{-1} taken as that of 2-C_5H_{11} + CH_3 (A_{-1} = 1.58E13), Ref : 17.

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Table 4.16 Thermochemical Database

			Cp							
SPECIES	Hf(298)	S(298)	300	400	500	600	800	1000	1500	COMMENTS
Ar	0.00	3.98	4.97	4.97	4.97	4.97	4.97	4.97	4.97	JANAF
H_2	0.00	31.21	6.90	6.95	6.99	7.02	7.10	7.21	7.22	JANAF
H	52.10	27.36	4.97	4.97	4.97	4.97	4.97	4.97.	4.97	JANAF
Cl	28.90	39.50	5.20	5.34	5.40	5.41	5.35	5.30	5.24	BSN
Cl_2	0.00	53.30	8.10	8.38	8.58	8.74	8.91	8.99	9.10	BSN
HCl	-22.07	44.60	6.96	6.95	6.99	7.07	7.29	7.56	8.10	SWS
CH_3	35.12	46.38	9.26	10.00	10.81	11.54	12.90	14.09	16.26	JANAF
CH_4	-17.90	44.48	8.51	9.77	11.10	12.44	15.00	17.20	20.61	JANAF
C_2H	132.00	49.58	9.02	9.63	10.18	10.67	11.48	12.10	12.94	FIELD87
C_2H_2	54.19	48.01	10.60	11.93	13.02	13.93	15.34	16.39	18.21	JANAF
C_2H_3	71.00	56.20	10.89	12.47	13.87	15.11	17.15	18.73	21.34	MG
C_2H_4	12.54	52.39	10.28	12.73	14.91	16.84	20.02	22.45	26.21	JANAF
C_2H_5	28.36	57.91	12.29	14.84	17.16	19.26	22.86	25.74	30.51	BLP
C_2H_6	-20.24	54.86	12.58	15.81	18.73	21.37	25.84	29.36	34.94	JANAF
CCl_3	19.00	72.05	15.99	17.05	17.93	18.47	19.08	19.27	19.56	BSN,RADI
CCl_4	-22.90	74.20	19.91	21.70	22.96	23.22	24.67	24.95	25.51	SWS
C_2Cl	125.99	59.33	11.51	11.99	12.43	12.82	13.50	14.04	15.01	BOZ
C_2Cl_2	50.10	65.00	15.80	16.91	17.74	18.37	19.16	19.60	20.22	BOZ
C_2Cl_3	53.02	79.16	18.60	20.44	21.69	22.58	23.70	24.46	25.32	JANAF
C_2Cl_4	-3.40	81.46	22.75	24.99	26.68	27.92	29.39	30.00	30.52	SWS
CHCl	76.62	56.17	8.80	9.45	10.13	10.81	12.11	13.22	14.78	LKL
CH_2Cl	29.10	58.58	9.92	11.14	12.37	13.44	14.59	14.69	16.79	ROUX,RADI
$CHCl_2$	23.50	66.73	12.30	13.90	14.90	15.44	16.78	17.45	18.42	ROUX,RADI
CH_2Cl_2	-22.80	64.59	12.29	14.23	15.88	17.26	19.39	20.89	23.04	SWS
HCCCl	55.00	58.11	13.17	14.29	15.18	15.88	16.88	17.55	18.80	BOZ
C_2H_3Cl	8.40	63.09	12.33	15.31	17.73	19.67	22.47	24.26	26.88	BOZ, WANG
CH_2CCl_2	0.62	69.26	16.02	18.57	20.75	22.57	25.34	27.17	29.32	BOZ, WANG

Table 4.16 (Continued)

			Cp							
SPECIES	Hf(298)	S(298)	300	400	500	600	800	1000	1500	COMMENTS
CHClCHCl	0.75	69.26	16.02	18.57	20.75	22.57	25.34	27.17	29.32	BOZ, WANG
CH_2CCl	60.40	63.06	11.67	13.95	15.75	17.19	19.23	20.46	22.19	BD, RADI
CHCHCl	60.40	63.06	11.67	13.95	15.75	17.19	19.23	20.46	22.19	BD,RADI
$CHCCl_2$	58.20	69.53	15.63	17.77	19.24	20.31	21.75	22.69	23.65	BD,RADI
C_2HCl_3	-1.88	77.67	19.26	21.80	23.67	25.06	26.94	28.15	28.98	BOZ, WANG
CH_2ClCH_2	20.78	68.51	13.91	16.85	19.46	21.76	25.55	28.42	32.64	ROUX
$CHCl_2CH_2$	16.04	77.33	17.90	20.92	23.37	25.28	28.09	29.92	33.19	BD, RADI
$CH_2ClCHCl_2$	-34.70	81.43	21.31	24.85	27.65	29.81	33.00	35.03	38.91	BOZ, WANG
CH_2ClCCl_3	-37.20	86.02	26.14	29.58	32.25	3428	36.97	38.52	40.64	SWS
$CHCl_2CHCl_2$	-37.20	86.02	26.14	29.58	32.25	3428	36.97	38.52	40.64	SWS
$CHCl_2CCl_2$	5.80	87.81	24.20	26.69	28.54	29.95	31.85	32.92	34.58	BD, RADI
CH_3CHCl	18.07	67.32	14.12	17.12	19.71	21.93	25.47	28.13	32.30	ROUX
CH_3CCl_3	-33.84	76.55	22.02	25.70	28.55	30.89	34.08	35.98	38.91	BOZ, WANG
CH_3CCl_2	11.30	73.61	17.29	20.38	22.99	25.20	28.56	30.84	33.80	BOZ, WANG
CHClCCl	55.35	70.51	15.15	17.07	18.58	19.68	21.44	22.39	23.65	BD, RADI
C_2H_5Cl	-26.83	66.03	15.06	18.62	21.67	24.28	28.43	31.47	36.27	JANAF
CH_3CHCl_2	-31.10	73.05	18.18	21.82	24.93	27.41	31.11	33.57	37.80	BOZ, WANG
$CHCl_2CHCl$	9.80	82.12	20.97	23.75	25.78	27.82	29.66	31.12	33.96	BD, RADI
$CH_2ClCHCl$	11.49	75.51	17.77	20.37	22.54	24.30	27.04	29.12	33.94	BD, RADI
CH_2ClCC_2	7.05	81.30	20.82	23.48	25.47	27.03	29.41	30.93	33.86	BD, RADI
CCl_3CH_2	14.84	81.46	22.06	24.74	26.71	28.24	30.45	31.95	34.19	BD, RADI

Unit of Hf is Kal/mol , Unit of S and Cp is cal/mol K

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Table 4.16 Thermodynamic analysis for the mechanism

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	= HCCCL	+ HCL
Hf {Kcal/mol}	.700	55.000	-22.000
S {cal/mol K}	69.200	58.100	44.600

dHr {kcal/mol} (298K) =	32.30	dHr avg (298., 1500. K) =	31.79
dU (dE) {kcal/mol} (") =	31.71	dUr avg (298., 1500. K) =	30.00
dSr {cal/mol K} (") =	33.50	dSr avg (298., 1500. K) =	33.54
dGr {kcal/mol} (") =	22.31	dGr avg (298., 1500. K) =	1.63
Af/Ar (") =	3.157E+02	Af/Ar avg (298., 1500. K) =	1.068E+02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	3.231E+01	3.171E+01	3.352E+01	3.176E+02	2.225E+01
400.00	3.263E+01	3.184E+01	3.447E+01	3.827E+02	1.884E+01
500.00	3.282E+01	3.183E+01	3.490E+01	3.802E+02	1.537E+01
600.00	3.290E+01	3.171E+01	3.504E+01	3.411E+02	1.187E+01
800.00	3.280E+01	3.121E+01	3.491E+01	2.390E+02	4.873E+00
1000.00	3.247E+01	3.048E+01	3.454E+01	1.590E+02	-2.074E+00
1200.00	3.202E+01	2.963E+01	3.413E+01	1.077E+02	-8.941E+00
1500.00	3.128E+01	2.830E+01	3.358E+01	6.533E+01	-1.909E+01
2000.00	3.007E+01	2.610E+01	3.289E+01	3.458E+01	-3.570E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	= CHCHCL	+ CL
Hf {Kcal/mol}	.700	63.300	28.900
S {cal/mol K}	69.200	62.300	39.500

dHr {kcal/mol} (298K) =	91.50	dHr avg (298., 1500. K) =	91.31
dU (dE) {kcal/mol} (") =	90.91	dUr avg (298., 1500. K) =	89.53
dSr {cal/mol K} (") =	32.60	dSr avg (298., 1500. K) =	32.72
dGr {kcal/mol} (") =	81.78	dGr avg (298., 1500. K) =	61.90
Af/Ar (") =	2.007E+02	Af/Ar avg (298., 1500. K) =	7.066E+01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	9.150E+01	9.091E+01	3.261E+01	2.003E+02	8.172E+01
400.00	9.164E+01	9.085E+01	3.301E+01	1.835E+02	7.844E+01
500.00	9.175E+01	9.076E+01	3.326E+01	1.671E+02	7.512E+01
600.00	9.183E+01	9.064E+01	3.341E+01	1.498E+02	7.179E+01
800.00	9.187E+01	9.028E+01	3.347E+01	1.157E+02	6.510E+01
1000.00	9.175E+01	8.977E+01	3.334E+01	8.675E+01	5.841E+01
1200.00	9.153E+01	8.915E+01	3.314E+01	6.532E+01	5.177E+01
1500.00	9.113E+01	8.815E+01	3.284E+01	4.496E+01	4.187E+01
2000.00	9.045E+01	8.648E+01	3.245E+01	2.770E+01	2.556E+01

Table 4.16 (Continued)

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	+ HCL	= CH2CL	+ CHCL2
Hf {Kcal/mol}	.700	-22.000	29.100	23.500
S {cal/mol K}	69.200	44.600	58.500	66.700

dHr {kcal/mol} (298K) =	73.90	dHr avg (298., 1500. K) =	73.28
dU (dE) {kcal/mol} (") =	73.90	dUr avg (298., 1500. K) =	73.28
dSr {cal/mol K} (") =	11.40	dSr avg (298., 1500. K) =	10.75
dGr {kcal/mol} (") =	70.50	dGr avg (298., 1500. K) =	63.62
Af/Ar (") =	3.102E+02	Af/Ar avg (298., 1500. K) =	2.236E+02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	7.390E+01	7.390E+01	1.140E+01	3.097E+02	7.048E+01
400.00	7.386E+01	7.386E+01	1.129E+01	2.929E+02	6.935E+01
500.00	7.383E+01	7.383E+01	1.122E+01	2.839E+02	6.822E+01
600.00	7.380E+01	7.380E+01	1.116E+01	2.750E+02	6.710E+01
800.00	7.367E+01	7.367E+01	1.098E+01	2.506E+02	6.489E+01
1000.00	7.344E+01	7.344E+01	1.073E+01	2.209E+02	6.272E+01
1200.00	7.315E+01	7.315E+01	1.046E+01	1.930E+02	6.060E+01
1500.00	7.267E+01	7.267E+01	1.010E+01	1.612E+02	5.752E+01
2000.00	7.184E+01	7.184E+01	9.622E+00	1.268E+02	5.259E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	+ HCL	= CHCL2CH2	+ CL
Hf {Kcal/mol}	.700	-22.000	16.000	28.900
S {cal/mol K}	69.200	44.600	77.300	39.500

dHr {kcal/mol} (298K) =	66.20	dHr avg (298., 1500. K) =	66.68
dU (dE) {kcal/mol} (") =	66.20	dUr avg (298., 1500. K) =	66.68
dSr {cal/mol K} (") =	3.00	dSr avg (298., 1500. K) =	3.63
dGr {kcal/mol} (") =	65.31	dGr avg (298., 1500. K) =	63.42
Af/Ar (") =	4.526E+00	Af/Ar avg (298., 1500. K) =	6.222E+00

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	6.620E+01	6.620E+01	3.003E+00	4.532E+00	6.530E+01
400.00	6.626E+01	6.626E+01	3.172E+00	4.936E+00	6.499E+01
500.00	6.634E+01	6.634E+01	3.356E+00	5.413E+00	6.467E+01
600.00	6.643E+01	6.643E+01	3.521E+00	5.882E+00	6.432E+01
800.00	6.661E+01	6.661E+01	3.773E+00	6.677E+00	6.359E+01
1000.00	6.676E+01	6.676E+01	3.941E+00	7.269E+00	6.282E+01
1200.00	6.690E+01	6.690E+01	4.072E+00	7.763E+00	6.202E+01
1500.00	6.716E+01	6.716E+01	4.265E+00	8.554E+00	6.077E+01
2000.00	6.772E+01	6.772E+01	4.583E+00	1.004E+01	5.855E+01

Table 4.16 (Continued)

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	+ HCL	= CH2CLCHCL	+ CL
Hf {Kcal/mol}	.700	-22.000	11.400	28.900
S {cal/mol K}	69.200	44.600	75.700	39.500

dHr {kcal/mol} (298K) = 61.60 dHr avg (298., 1500. K) = 61.79
dU (dE) {kcal/mol} (") = 61.60 dUr avg (298., 1500. K) = 61.79
dSr {cal/mol K} (") = 1.40 dSr avg (298., 1500. K) = 1.56
dGr {kcal/mol} (") = 61.18 dGr avg (298., 1500. K) = 60.39
Af/Ar (") = 2.023E+00 Af/Ar avg (298., 1500. K) = 2.187E+00

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	6.160E+01	6.160E+01	1.401E+00	2.024E+00	6.118E+01
400.00	6.161E+01	6.161E+01	1.429E+00	2.053E+00	6.104E+01
500.00	6.161E+01	6.161E+01	1.426E+00	2.049E+00	6.090E+01
600.00	6.160E+01	6.160E+01	1.412E+00	2.036E+00	6.075E+01
800.00	6.159E+01	6.159E+01	1.396E+00	2.019E+00	6.047E+01
1000.00	6.162E+01	6.162E+01	1.425E+00	2.048E+00	6.019E+01
1200.00	6.171E+01	6.171E+01	1.508E+00	2.136E+00	5.990E+01
1500.00	6.198E+01	6.198E+01	1.711E+00	2.365E+00	5.942E+01
2000.00	6.264E+01	6.264E+01	2.083E+00	2.853E+00	5.847E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	+ CL	= CHCLCCL	+ HCL
Hf {Kcal/mol}	.700	28.900	55.300	-22.000
S {cal/mol K}	69.200	39.500	70.500	44.600

dHr {kcal/mol} (298K) = 3.70 dHr avg (298., 1500. K) = 2.82
dU (dE) {kcal/mol} (") = 3.70 dUr avg (298., 1500. K) = 2.82
dSr {cal/mol K} (") = 6.40 dSr avg (298., 1500. K) = 5.67
dGr {kcal/mol} (") = 1.79 dGr avg (298., 1500. K) = -2.28
Af/Ar (") = 2.505E+01 Af/Ar avg (298., 1500. K) = 1.734E+01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	3.702E+00	3.702E+00	6.408E+00	2.515E+01	1.780E+00
400.00	3.797E+00	3.797E+00	6.685E+00	2.892E+01	1.123E+00
500.00	3.822E+00	3.822E+00	6.744E+00	2.979E+01	4.501E-01
600.00	3.785E+00	3.785E+00	6.679E+00	2.882E+01	-2.219E-01
800.00	3.556E+00	3.556E+00	6.356E+00	2.450E+01	-1.528E+00
1000.00	3.176E+00	3.176E+00	5.933E+00	1.981E+01	-2.758E+00
1200.00	2.705E+00	2.705E+00	5.506E+00	1.597E+01	-3.901E+00
1500.00	1.942E+00	1.942E+00	4.938E+00	1.200E+01	-5.465E+00
2000.00	6.777E-01	6.777E-01	4.210E+00	8.321E+00	-7.743E+00

Table 4.16 (Continued)

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCHCL	+ CL	= CHCHCL	+ CL2
Hf {Kcal/mol}	.700	28.900	63.300	.000
S {cal/mol K}	69.200	39.500	62.300	53.300

dHr {kcal/mol} (298K) = 33.70 dHr avg (298., 1500. K) = 32.44
dU (dE) {kcal/mol} (") = 33.70 dUr avg (298., 1500. K) = 32.44
dSr {cal/mol K} (") = 6.90 dSr avg (298., 1500. K) = 5.47
dGr {kcal/mol} (") = 31.64 dGr avg (298., 1500. K) = 27.52
Af/Ar (") = 3.222E+01 Af/Ar avg (298., 1500. K) = 1.569E+01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	3.370E+01	3.370E+01	6.894E+00	3.212E+01	3.163E+01
400.00	3.360E+01	3.360E+01	6.616E+00	2.792E+01	3.096E+01
500.00	3.350E+01	3.350E+01	6.387E+00	2.489E+01	3.031E+01
600.00	3.338E+01	3.338E+01	6.163E+00	2.223E+01	2.968E+01
800.00	3.304E+01	3.304E+01	5.682E+00	1.745E+01	2.849E+01
1000.00	3.258E+01	3.258E+01	5.171E+00	1.350E+01	2.741E+01
1200.00	3.204E+01	3.204E+01	4.677E+00	1.053E+01	2.642E+01
1500.00	3.118E+01	3.118E+01	4.041E+00	7.643E+00	2.512E+01
2000.00	2.979E+01	2.979E+01	3.240E+00	5.107E+00	2.331E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCHCL	= C2H2	+ CL
Hf {Kcal/mol}	63.300	54.100	28.900
S {cal/mol K}	62.300	48.000	39.500

dHr {kcal/mol} (298K) = 19.70 dHr avg (298., 1500. K) = 20.43
dU (dE) {kcal/mol} (") = 19.11 dUr avg (298., 1500. K) = 18.64
dSr {cal/mol K} (") = 25.20 dSr avg (298., 1500. K) = 26.46
dGr {kcal/mol} (") = 12.19 dGr avg (298., 1500. K) = -3.36
Af/Ar (") = 4.843E+00 Af/Ar avg (298., 1500. K) = 3.028E+00

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	1.971E+01	1.911E+01	2.522E+01	4.870E+00	1.214E+01
400.00	2.002E+01	1.923E+01	2.615E+01	5.811E+00	9.567E+00
500.00	2.025E+01	1.925E+01	2.664E+01	5.975E+00	6.925E+00
600.00	2.040E+01	1.921E+01	2.693E+01	5.755E+00	4.245E+00
800.00	2.061E+01	1.902E+01	2.723E+01	5.024E+00	-1.176E+00
1000.00	2.077E+01	1.878E+01	2.741E+01	4.386E+00	-6.641E+00
1200.00	2.092E+01	1.854E+01	2.755E+01	3.920E+00	-1.214E+01
1500.00	2.115E+01	1.817E+01	2.772E+01	3.421E+00	-2.043E+01
2000.00	2.152E+01	1.754E+01	2.793E+01	2.854E+00	-3.434E+01

Table 4.16 (Continued)

THERMODYNAMIC ANALYSIS for REACTION

Rx	CHCLCCL	= HCCCL	+ CL
Hf {Kcal/mol}	55.300	55.000	28.900
S {cal/mol K}	70.500	58.100	39.500

dHr {kcal/mol} (298K) =	28.60	dHr avg (298., 1500. K) =	28.97
dU (dE) {kcal/mol} (") =	28.01	dUr avg (298., 1500. K) =	27.18
dSr {cal/mol K} (") =	27.10	dSr avg (298., 1500. K) =	27.87
dGr {kcal/mol} (") =	20.52	dGr avg (298., 1500. K) =	3.91
Af/Ar (") =	1.260E+01	Af/Ar avg (298., 1500. K) =	6.160E+00

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	2.860E+01	2.801E+01	2.712E+01	1.263E+01	2.047E+01
400.00	2.883E+01	2.804E+01	2.778E+01	1.323E+01	1.772E+01
500.00	2.900E+01	2.801E+01	2.815E+01	1.276E+01	1.492E+01
600.00	2.912E+01	2.792E+01	2.836E+01	1.183E+01	1.210E+01
800.00	2.924E+01	2.765E+01	2.855E+01	9.755E+00	6.401E+00
1000.00	2.929E+01	2.731E+01	2.861E+01	8.025E+00	6.840E-01
1200.00	2.931E+01	2.693E+01	2.863E+01	6.745E+00	-5.040E+00
1500.00	2.933E+01	2.635E+01	2.864E+01	5.442E+00	-1.363E+01
2000.00	2.940E+01	2.542E+01	2.868E+01	4.156E+00	-2.796E+01

THERMODYNAMIC ANALYSIS for REACTION

Rx	CH2CLCHCL2	= CH2CLCHCL	+ CL
Hf {Kcal/mol}	-34.700	11.400	28.900
S {cal/mol K}	81.400	75.700	39.500

dHr {kcal/mol} (298K) =	75.00	dHr avg (298., 1500. K) =	74.71
dU (dE) {kcal/mol} (") =	74.41	dUr avg (298., 1500. K) =	72.92
dSr {cal/mol K} (") =	33.80	dSr avg (298., 1500. K) =	33.58
dGr {kcal/mol} (") =	64.92	dGr avg (298., 1500. K) =	44.52
Af/Ar (") =	3.671E+02	Af/Ar avg (298., 1500. K) =	1.092E+02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	7.500E+01	7.441E+01	3.381E+01	3.666E+02	6.486E+01
400.00	7.510E+01	7.430E+01	3.409E+01	3.168E+02	6.146E+01
500.00	7.511E+01	7.412E+01	3.412E+01	2.571E+02	5.805E+01
600.00	7.507E+01	7.388E+01	3.404E+01	2.063E+02	5.464E+01
800.00	7.491E+01	7.332E+01	3.382E+01	1.380E+02	4.785E+01
1000.00	7.474E+01	7.275E+01	3.363E+01	1.002E+02	4.111E+01
1200.00	7.459E+01	7.221E+01	3.349E+01	7.819E+01	3.440E+01
1500.00	7.442E+01	7.144E+01	3.337E+01	5.866E+01	2.437E+01
2000.00	7.416E+01	7.019E+01	3.322E+01	4.078E+01	7.729E+00

Table 4.16 (Continued)

THERMODYNAMIC ANALYSIS for REACTION
Rx CH2CLCHCL2 = CH2CCL2 + HCL
Hf {Kcal/mol} -34.700 .600 -22.000
S {cal/mol K} 81.400 69.200 44.600

dHr {kcal/mol} (298K) = 13.30 dHr avg (298., 1500. K) = 12.82
dU (dE) {kcal/mol} (") = 12.71 dUr avg (298., 1500. K) = 11.03
dSr {cal/mol K} (") = 32.40 dSr avg (298., 1500. K) = 32.03
dGr {kcal/mol} (") = 3.64 dGr avg (298., 1500. K) = -15.98
Af/Ar (") = 1.815E+02 Af/Ar avg (298., 1500. K) = 4.990E+01

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	1.330E+01	1.271E+01	3.241E+01	1.811E+02	3.580E+00
400.00	1.339E+01	1.259E+01	3.266E+01	1.543E+02	3.238E-01
500.00	1.340E+01	1.241E+01	3.269E+01	1.255E+02	-2.945E+00
600.00	1.337E+01	1.217E+01	3.263E+01	1.013E+02	-6.212E+00
800.00	1.322E+01	1.163E+01	3.242E+01	6.836E+01	-1.272E+01
1000.00	1.302E+01	1.103E+01	3.220E+01	4.893E+01	-1.918E+01
1200.00	1.278E+01	1.040E+01	3.199E+01	3.661E+01	-2.560E+01
1500.00	1.234E+01	9.358E+00	3.166E+01	2.480E+01	-3.515E+01
2000.00	1.143E+01	7.452E+00	3.113E+01	1.43 0E+01	-5.084E+01

THERMODYNAMIC ANALYSIS for REACTION
Rx CH2CLCHCL2 = CHCL2CH2 + CL
Hf {Kcal/mol} -34.700 16.000 28.900
S {cal/mol K} 81.400 77.300 39.500

dHr {kcal/mol} (298K) = 79.60 dHr avg (298., 1500. K) = 79.60
dU (dE) {kcal/mol} (") = 79.01 dUr avg (298., 1500. K) = 77.81
dSr {cal/mol K} (") = 35.40 dSr avg (298., 1500. K) = 35.66
dGr {kcal/mol} (") = 69.05 dGr avg (298., 1500. K) = 47.54
Af/Ar (") = 8.213E+02 Af/Ar avg (298., 1500. K) = 3.105E+02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	7.960E+01	7.901E+01	3.541E+01	8.207E+02	6.898E+01
400.00	7.975E+01	7.895E+01	3.583E+01	7.617E+02	6.542E+01
500.00	7.984E+01	7.885E+01	3.605E+01	6.790E+02	6.182E+01
600.00	7.990E+01	7.871E+01	3.615E+01	5.960E+02	5.821E+01
800.00	7.993E+01	7.834E+01	3.619E+01	4.565E+02	5.097E+01
1000.00	7.988E+01	7.789E+01	3.614E+01	3.557E+02	4.374E+01
1200.00	7.979E+01	7.740E+01	3.606E+01	2.842E+02	3.652E+01
1500.00	7.960E+01	7.662E+01	3.592E+01	2.122E+02	2.572E+01
2000.00	7.925E+01	7.527E+01	3.572E+01	1.435E+02	7.813E+00

Table 4.16 (Continued)

THERMODYNAMIC ANALYSIS for REACTION

Rx	CH2CCL2	= HCCCL	+ HCL
Hf {Kcal/mol}	.600	55.000	-22.000
S {cal/mol K}	69.200	58.100	44.600

dHr {kcal/mol} (298K) =	32.40	dHr avg (298., 1500. K) =	31.89
dU (dE) {kcal/mol} (") =	31.81	dUr avg (298., 1500. K) =	30.10
dSr {cal/mol K} (") =	33.50	dSr avg (298., 1500. K) =	33.54
dGr {kcal/mol} (") =	22.41	dGr avg (298., 1500. K) =	1.73
Af/Ar (") =	3.157E+02	Af/Ar avg (298., 1500. K) =	1.068E+02

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300.00	3.241E+01	3.181E+01	3.352E+01	3.176E+02	2.235E+01
400.00	3.273E+01	3.194E+01	3.447E+01	3.827E+02	1.894E+01
500.00	3.292E+01	3.193E+01	3.490E+01	3.802E+02	1.547E+01
600.00	3.300E+01	3.181E+01	3.504E+01	3.411E+02	1.197E+01
800.00	3.290E+01	3.131E+01	3.491E+01	2.390E+02	4.973E+00
1000.00	3.257E+01	3.058E+01	3.454E+01	1.590E+02	-1.974E+00
1200.00	3.212E+01	2.973E+01	3.413E+01	1.077E+02	-8.841E+00
1500.00	3.138E+01	2.840E+01	3.358E+01	6.533E+01	-1.899E+01
2000.00	3.017E+01	2.620E+01	3.289E+01	3.458E+01	-3.560E+01

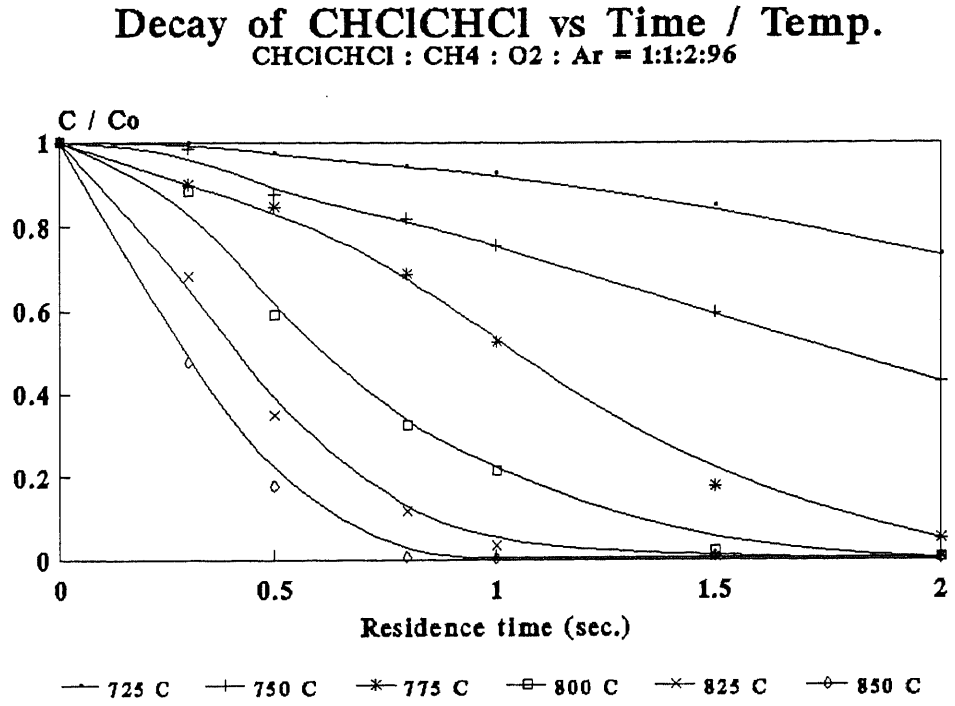


Figure 4.9

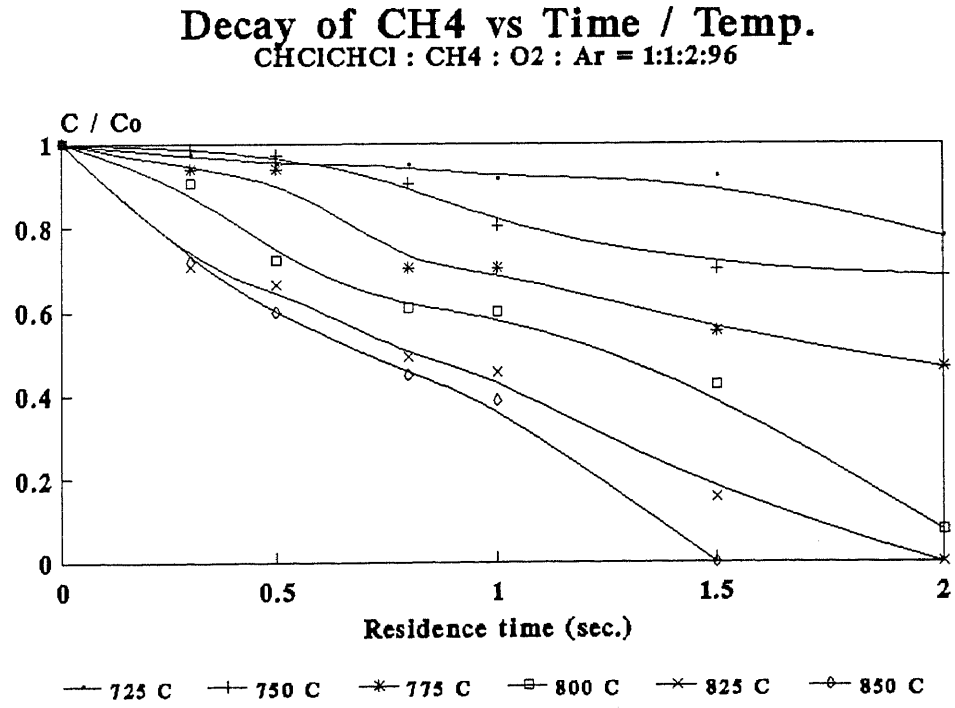


Figure 4.10

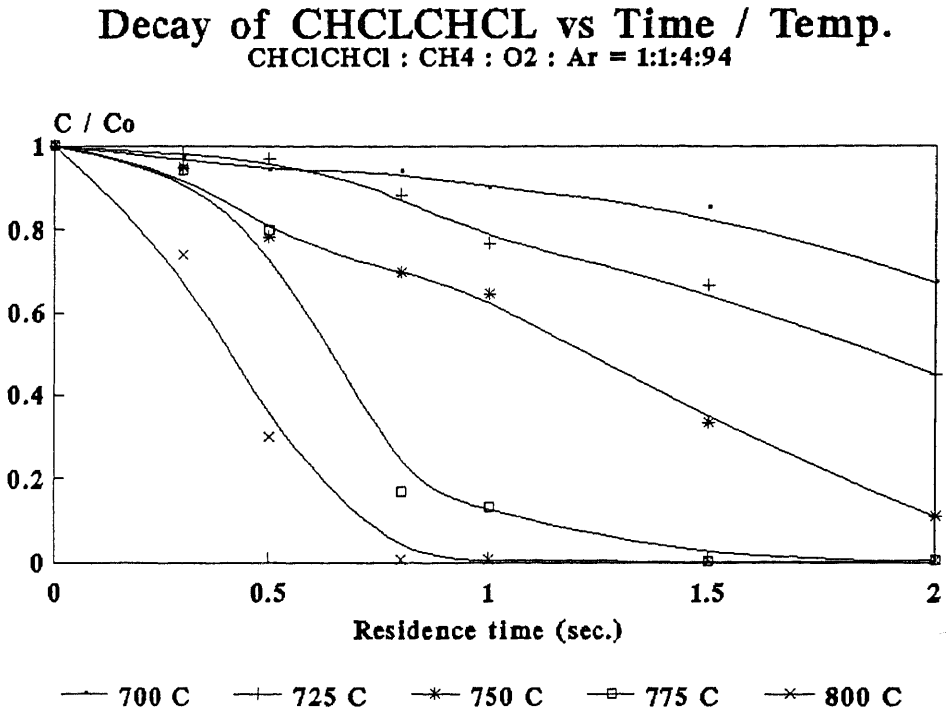


Figure 4.11

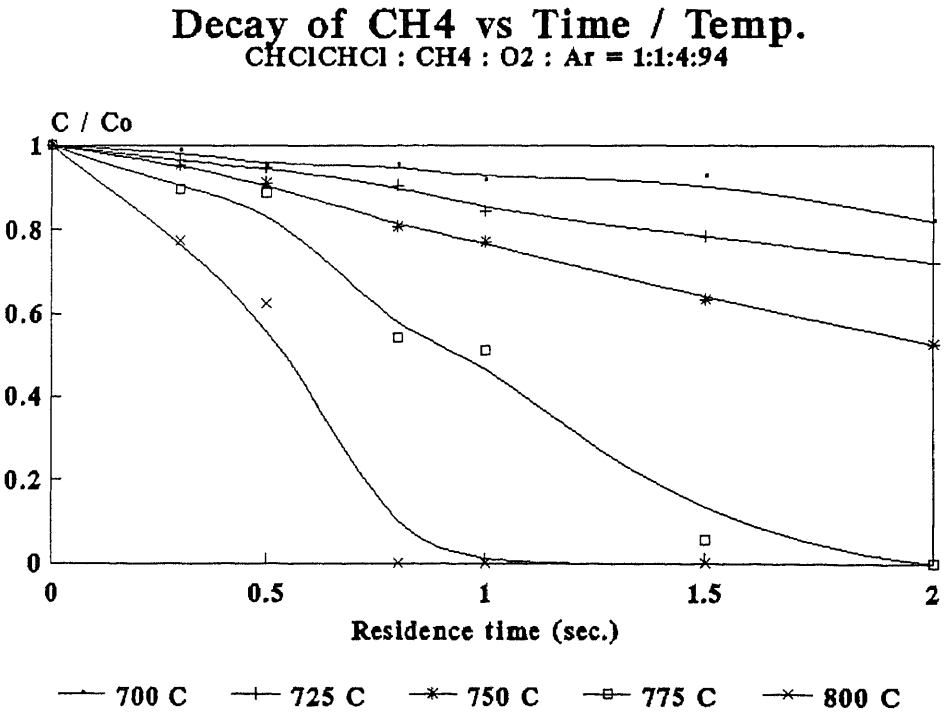


Figure 4.12

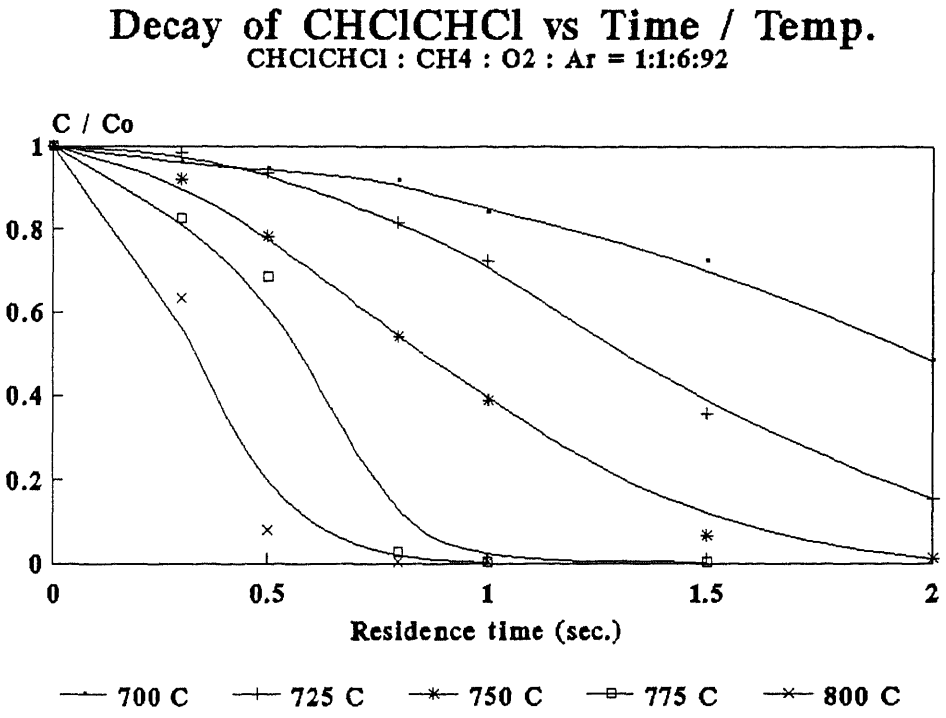


Figure 4.13

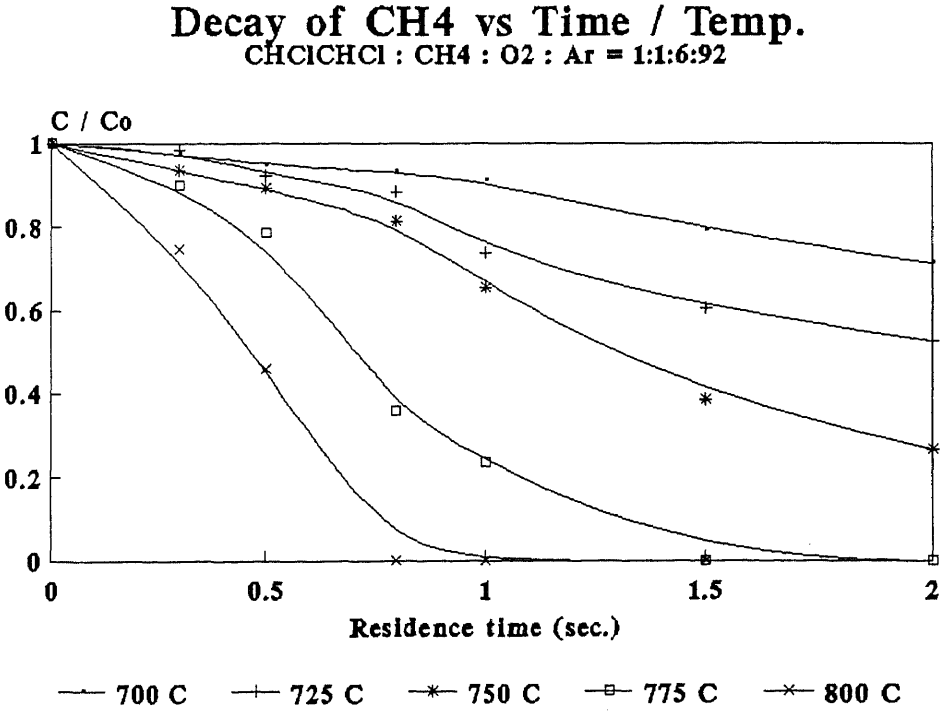


Figure 4.14

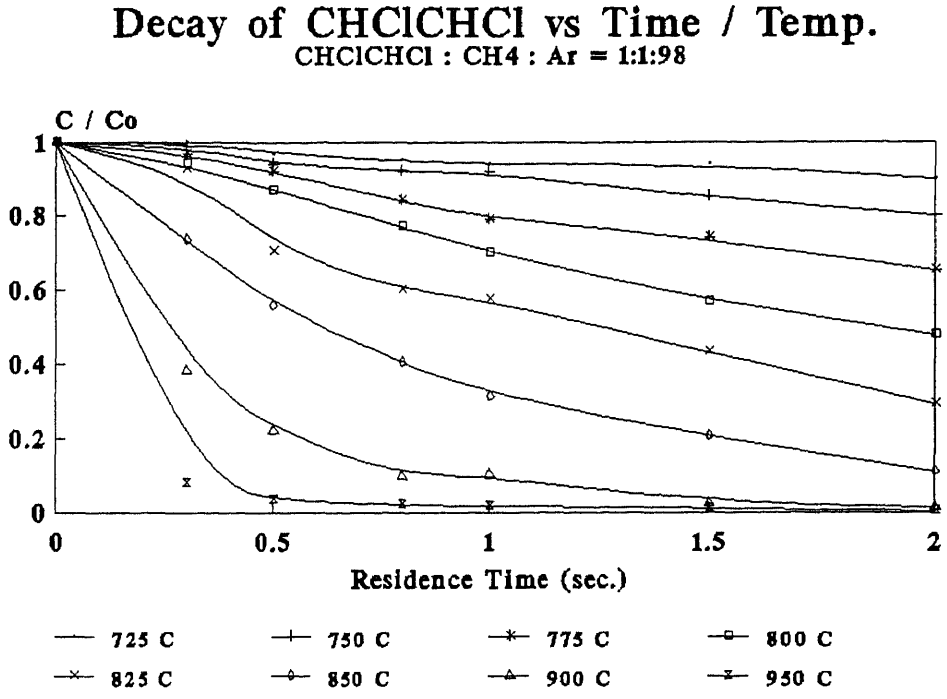


Figure 4.15

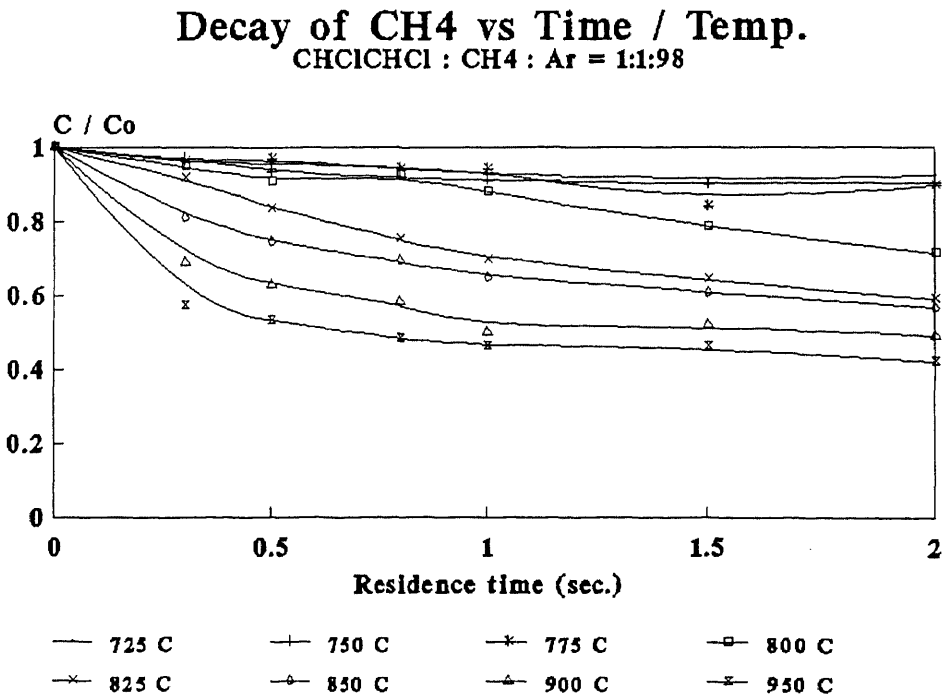


Figure 4.16

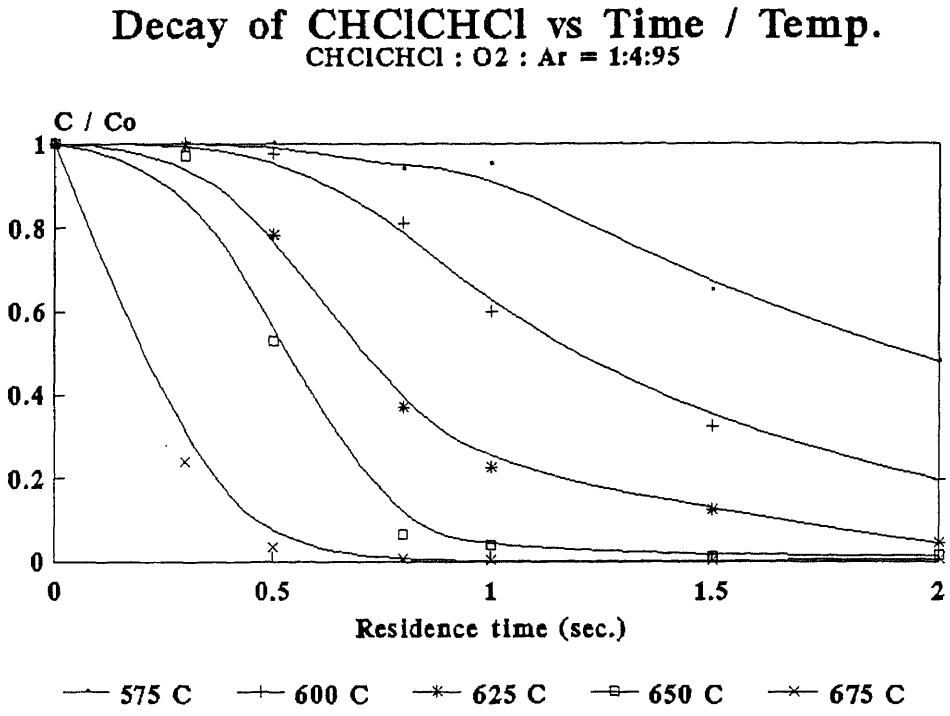


Figure 4.17

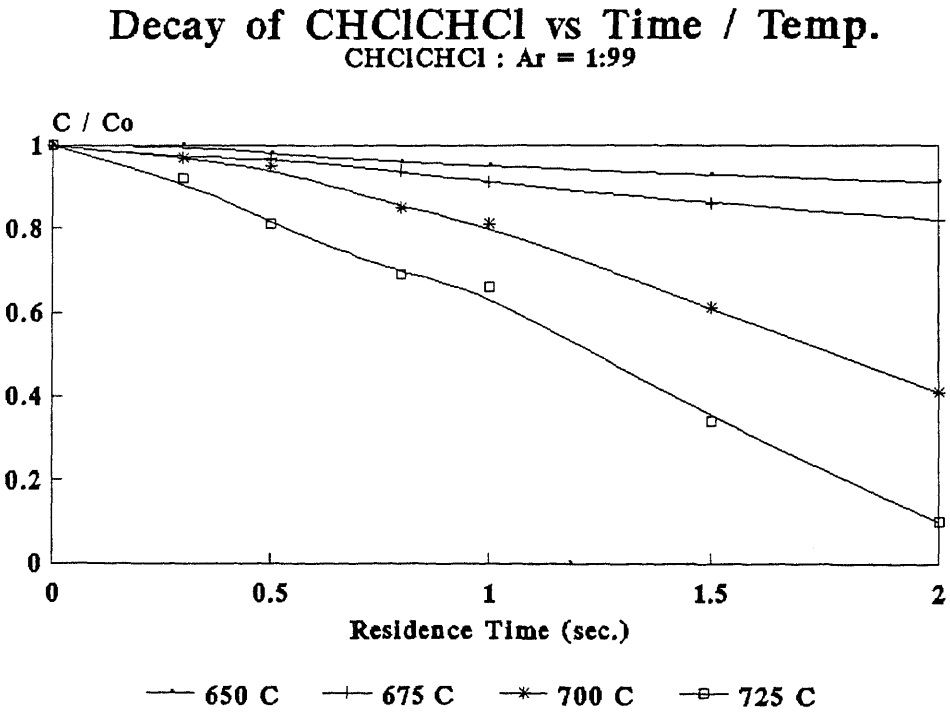


Figure 4.18

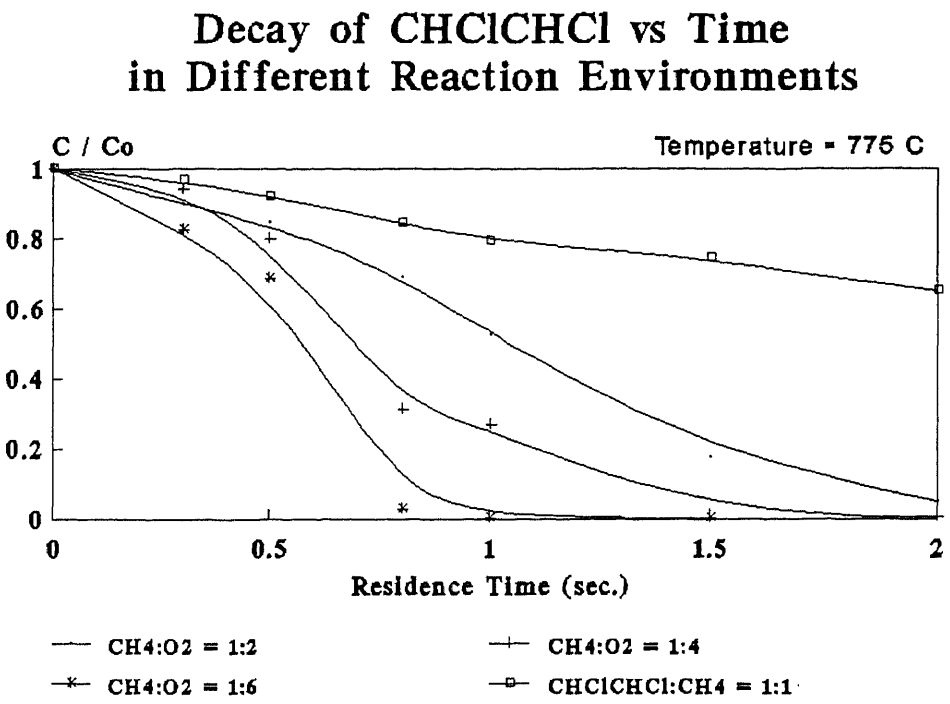


Figure 4.19

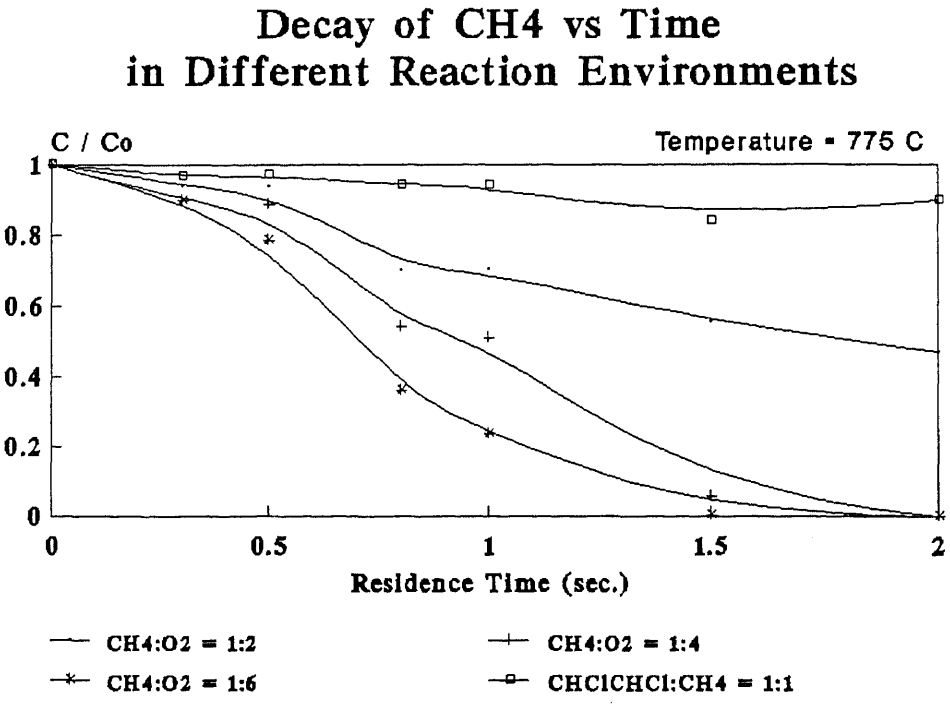


Figure 4.20

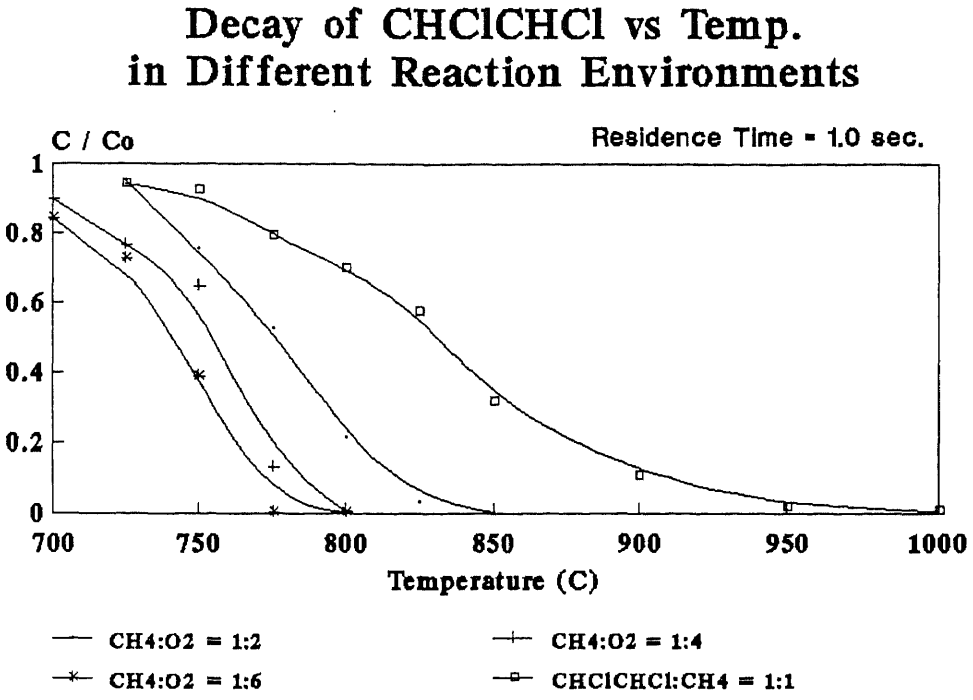


Figure 4.21

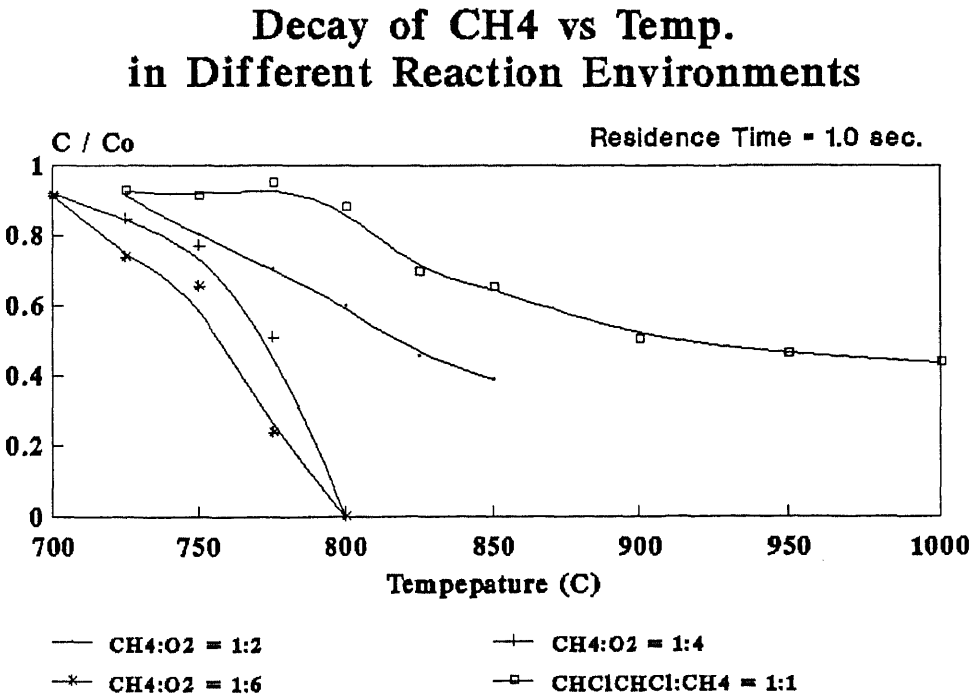


Figure 4.22

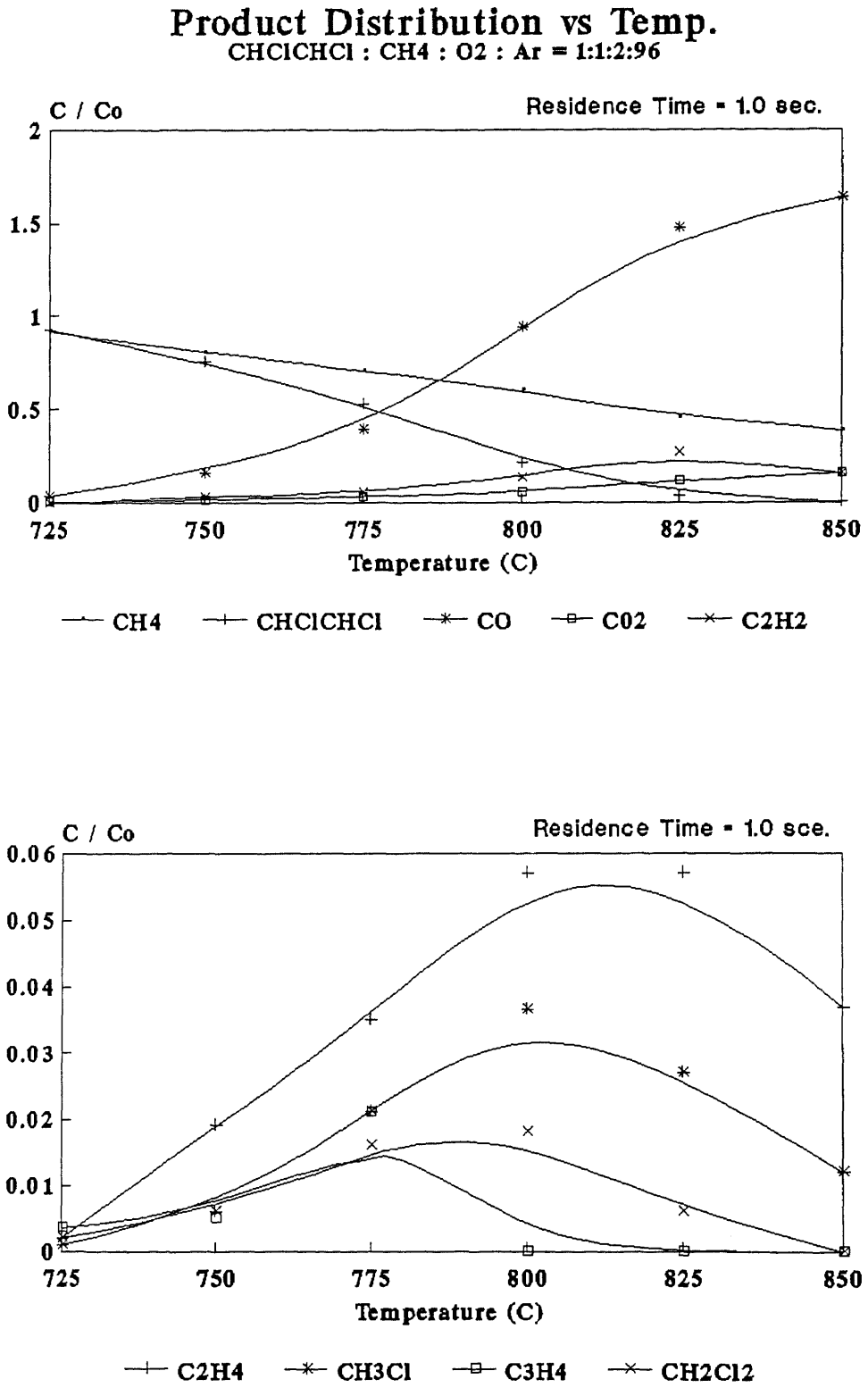

Product Distribution vs Temp.
CHClCHCl : CH4 : O2 : Ar = 1:1:2:96
C / Co
Residence Time = 1.0 sec.
2
1.5
1
0.5
0
725
750
775
800
825
850
Temperature (C)
CH4
CHClCHCl
CO
C02
C2H2
C / Co
Residence Time = 1.0 sec.
0.06
0.05
0.04
0.03
0.02
0.01
0
725
750
775
800
825
850
Temperature (C)
C2H4
CH3Cl
C3H4
CH2Cl2

Figure 4.23

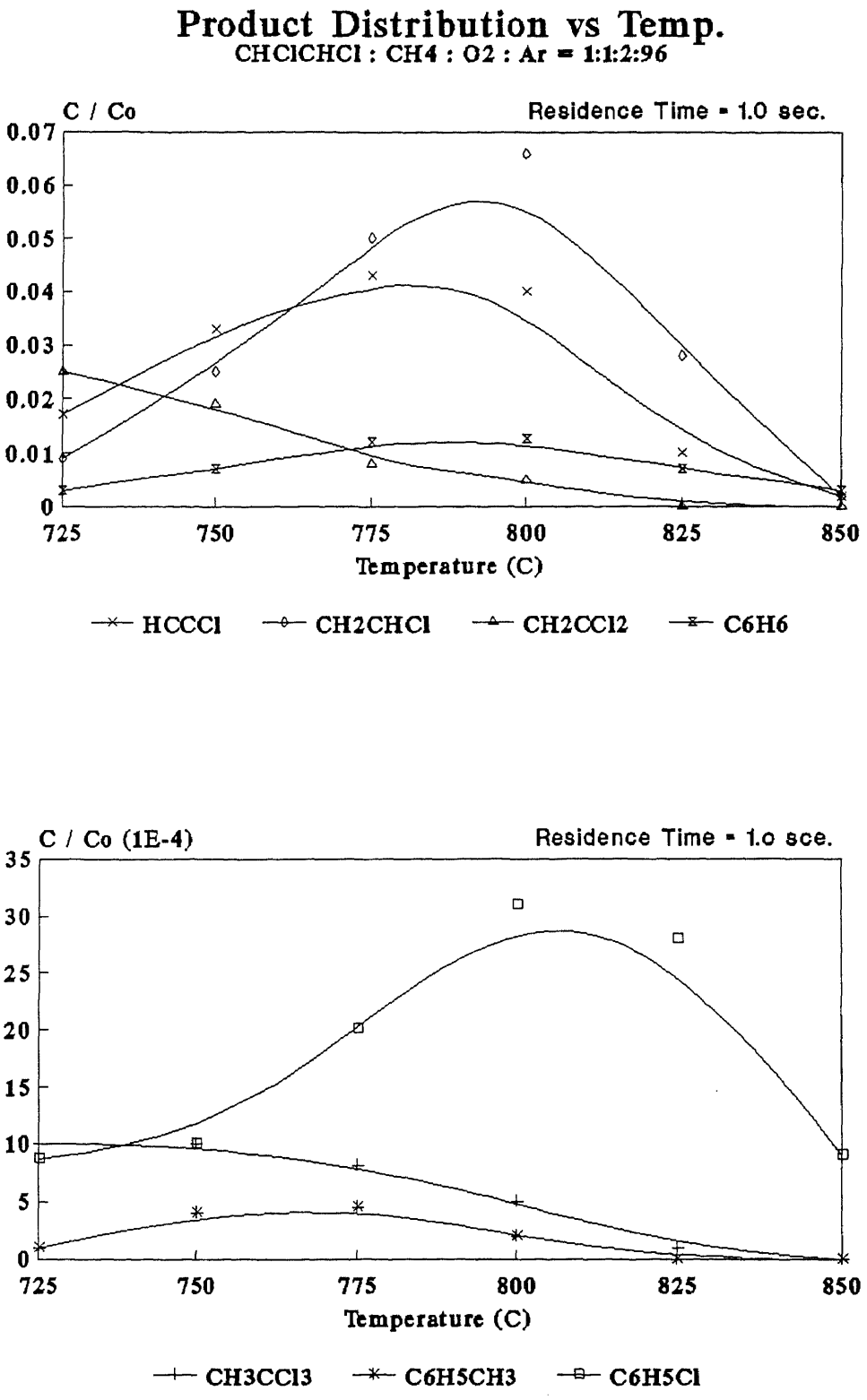

Product Distribution vs Temp.
CHClCHCl : CH4 : O2 : Ar = 1:1:2:96
C / Co
Residence Time = 1.0 sec.
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
725
750
775
800
825
850
Temperature (C)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co (1E-4)
Residence Time = 1.0 sec.
35
30
25
20
15
10
5
0
725
750
775
800
825
850
Temperature (C)
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.24

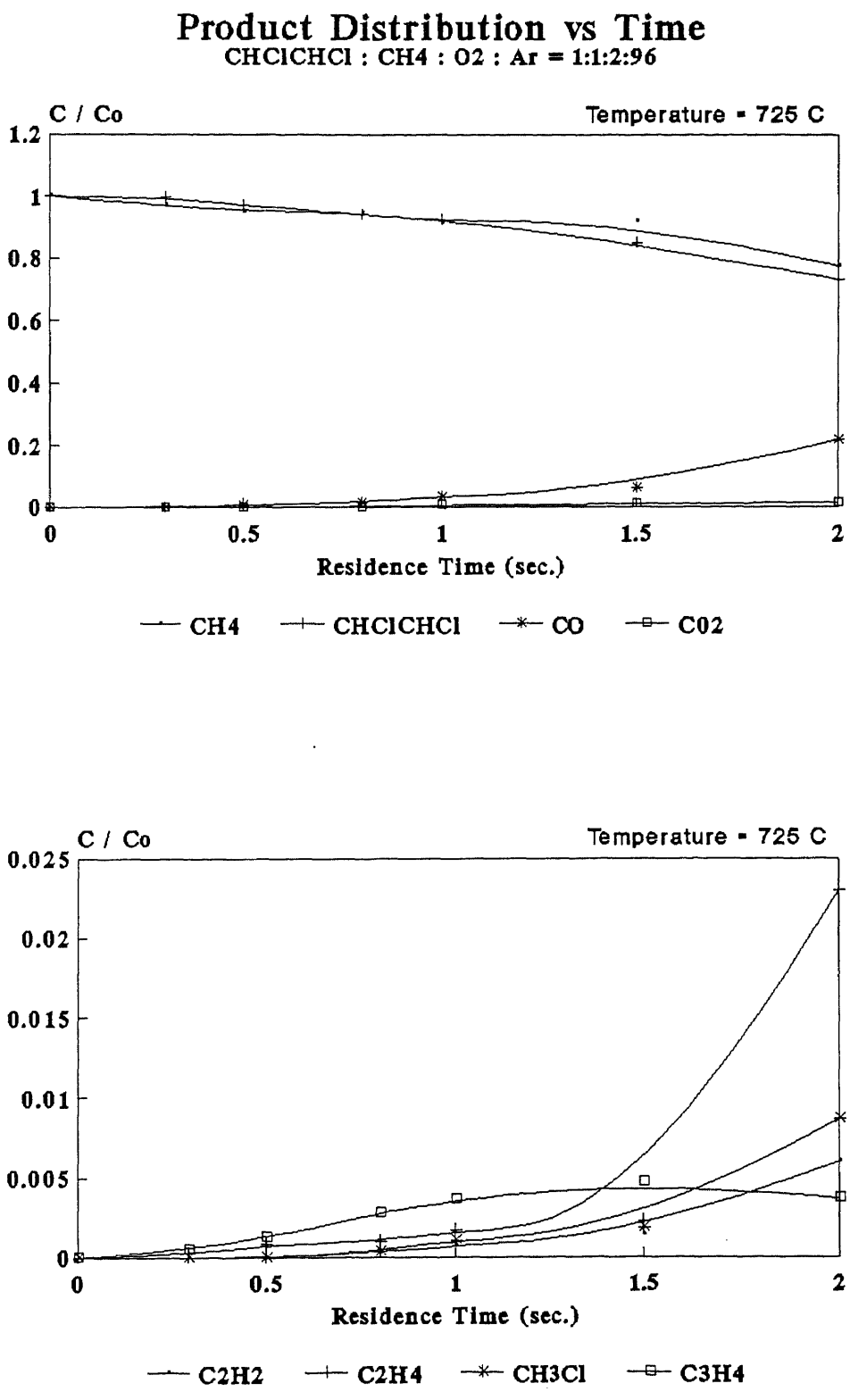

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:2:96
C / Co
Temperature = 725 C
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
CHClCHCl
CO
C02
C / Co
Temperature = 725 C
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.25

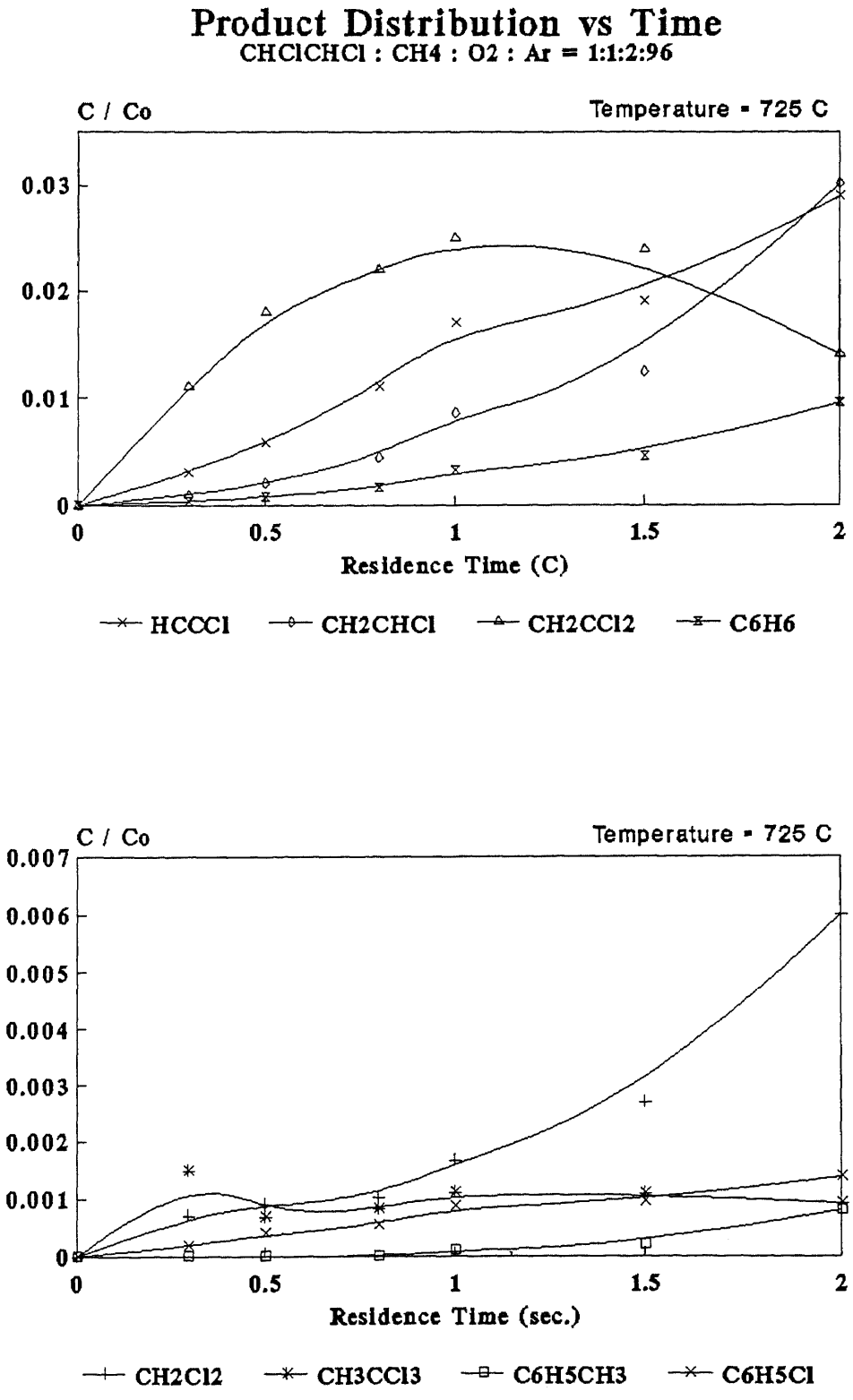

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:2:96
C / Co
Temperature = 725 C
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (C)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Temperature = 725 C
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.26

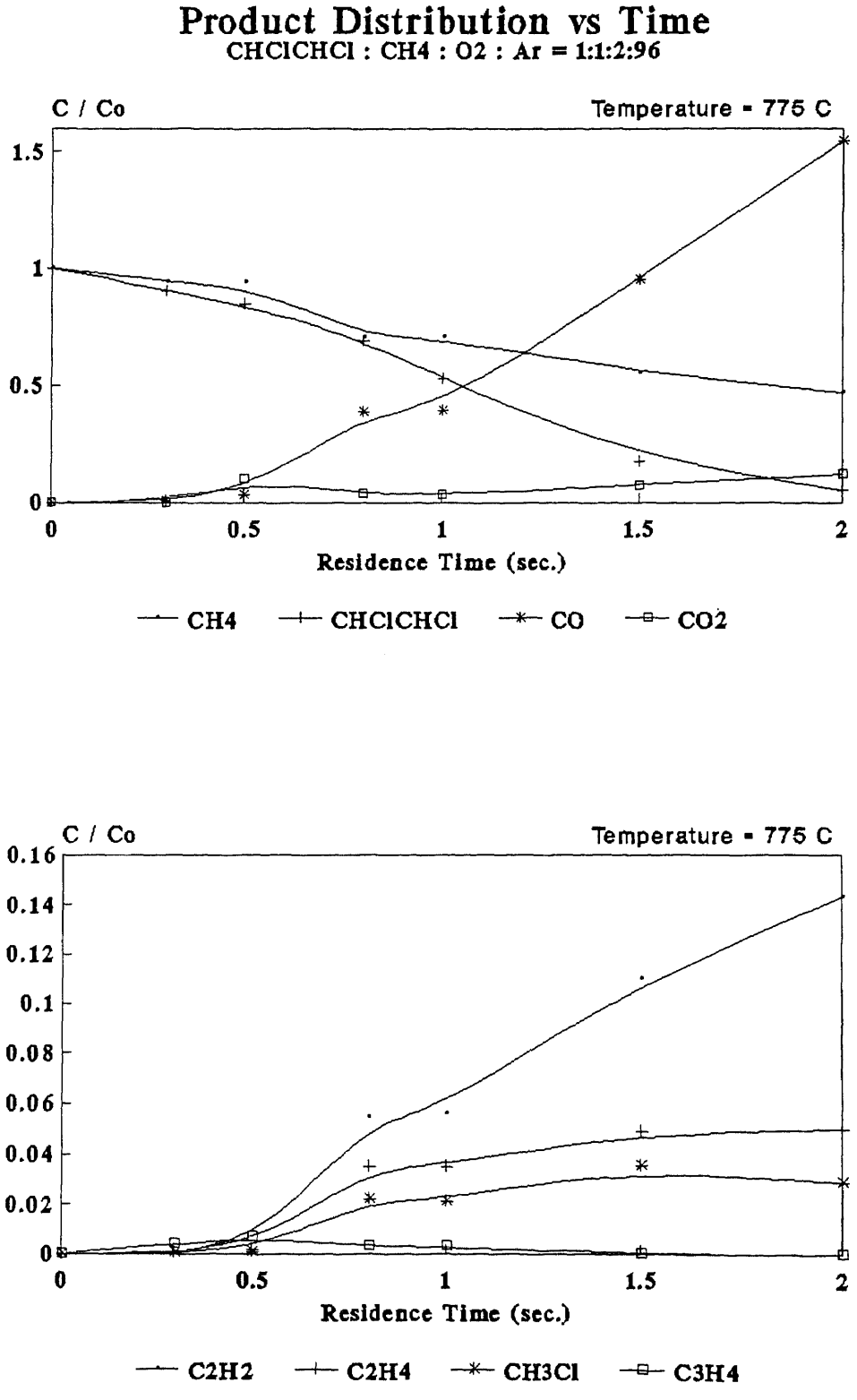

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:2:96
C / Co
Temperature = 775 C
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
CHClCHCl
CO
CO2
C / Co
Temperature = 775 C
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.27

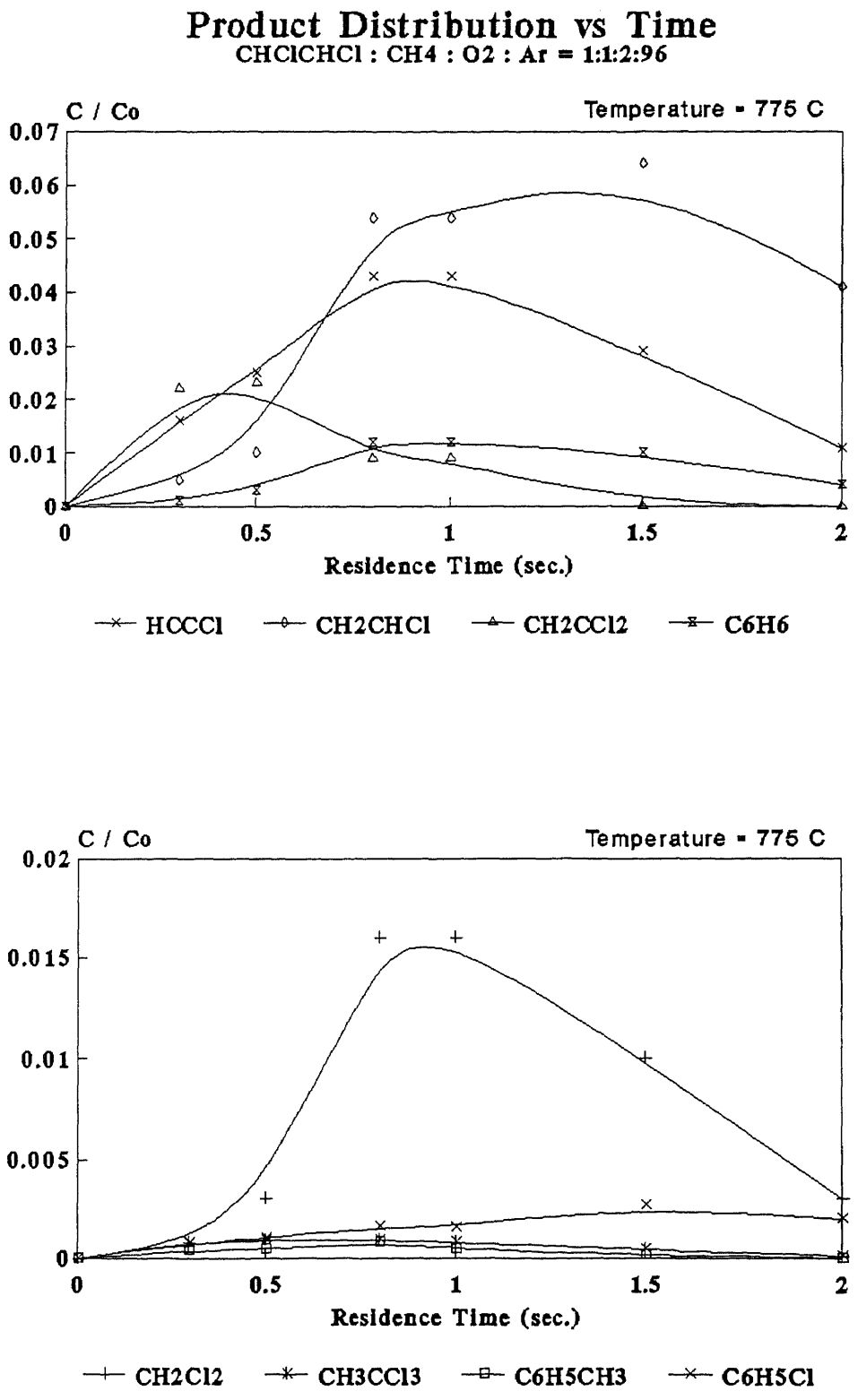

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:2:96
C / Co
Temperature = 775 C
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Temperature = 775 C
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.28

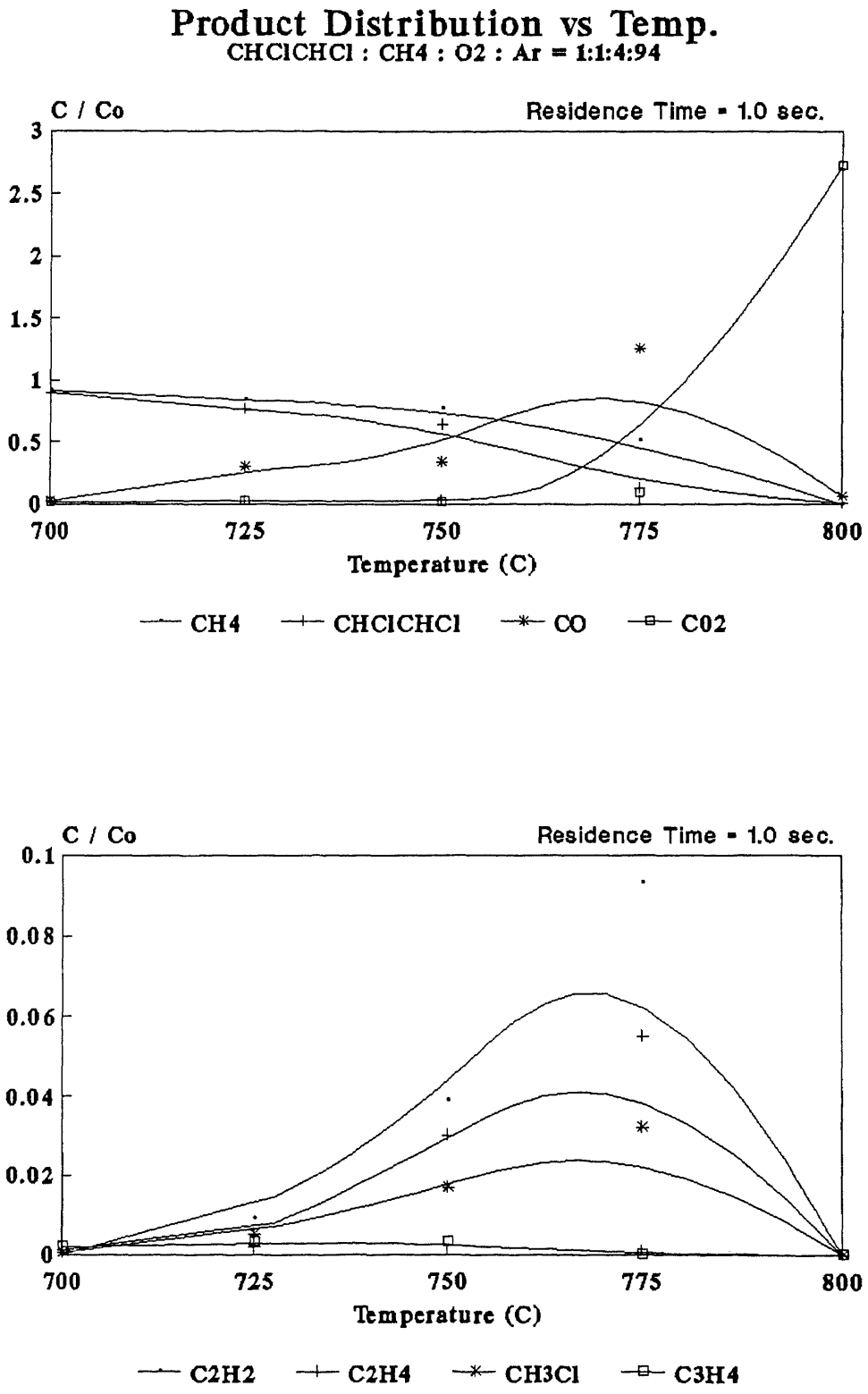

Product Distribution vs Temp.
CHClCHCl : CH4 : O2 : Ar = 1:1:4:94
C / Co
Residence Time = 1.0 sec.
3
2.5
2
1.5
1
0.5
0
700
725
750
775
800
Temperature (C)
CH4
CHClCHCl
CO
C02
C / Co
Residence Time = 1.0 sec.
0.1
0.08
0.06
0.04
0.02
0
700
725
750
775
800
Temperature (C)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.29

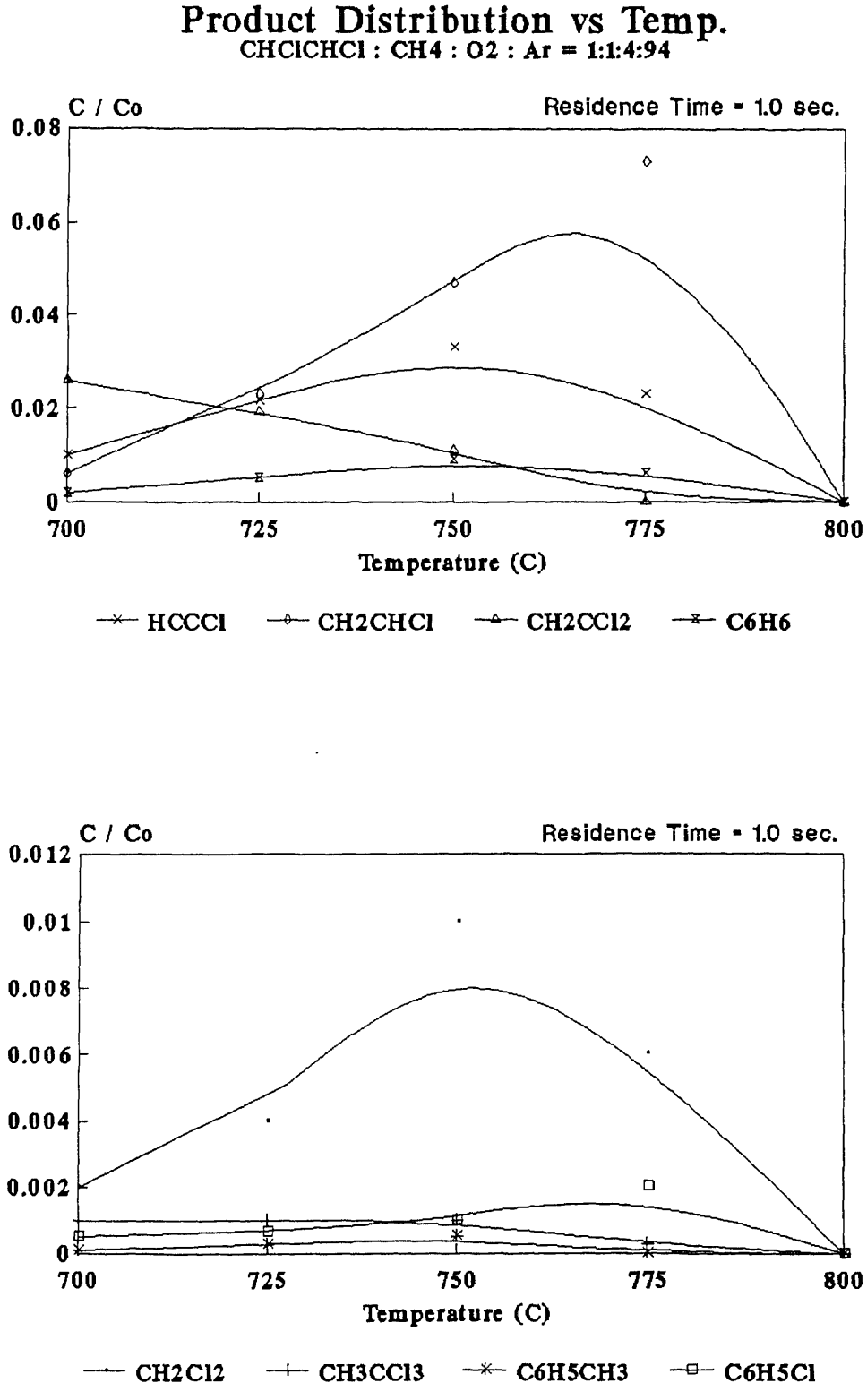

Product Distribution vs Temp.
CHClCHCl : CH4 : O2 : Ar = 1:1:4:94
C / Co
Residence Time = 1.0 sec.
0.08
0.06
0.04
0.02
0
700
725
750
775
800
Temperature (C)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Residence Time = 1.0 sec.
0.012
0.01
0.008
0.006
0.004
0.002
0
700
725
750
775
800
Temperature (C)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.30

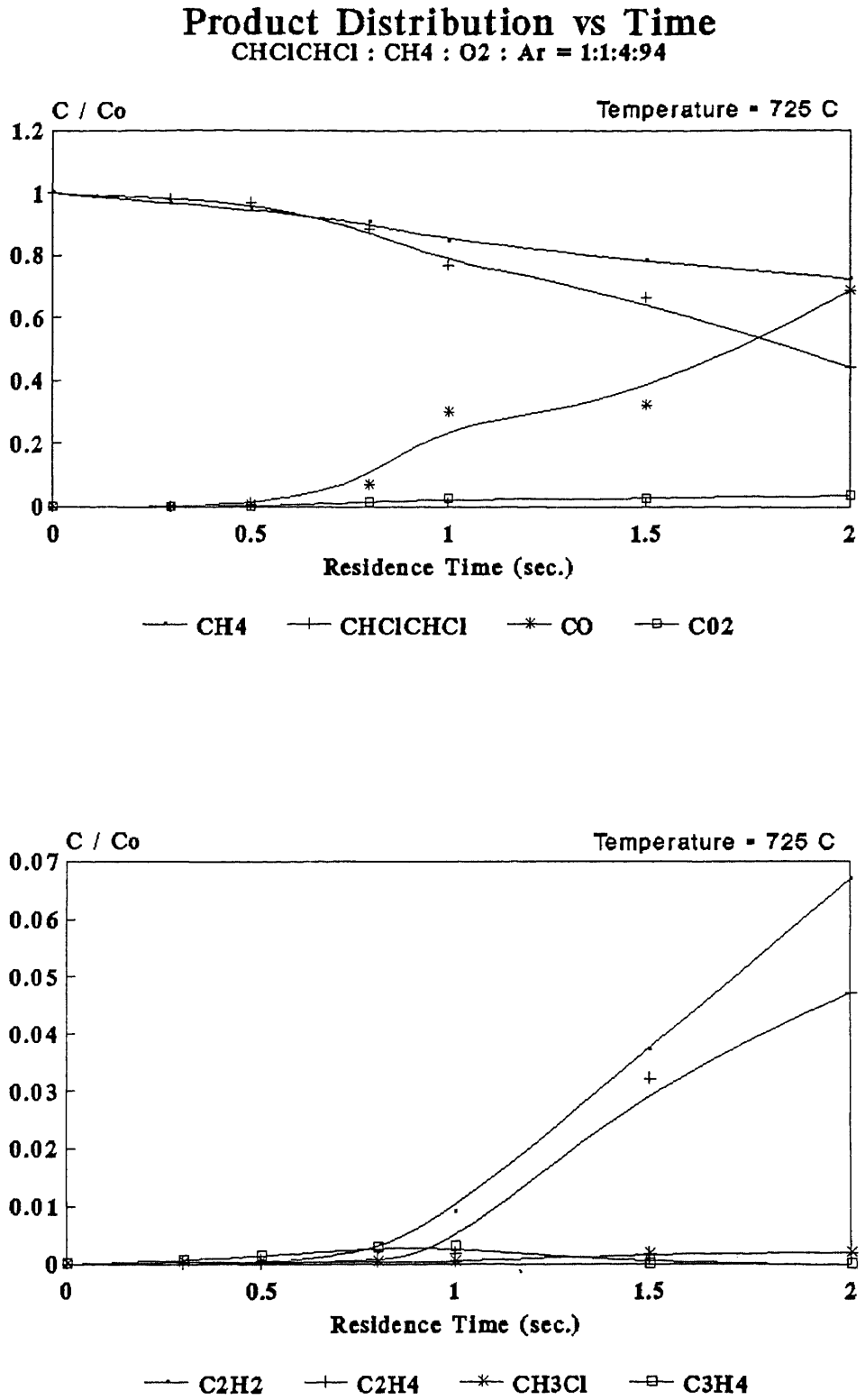

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:4:94
C / Co
Temperature = 725 C
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
CHClCHCl
CO
C02
C / Co
Temperature = 725 C
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.31

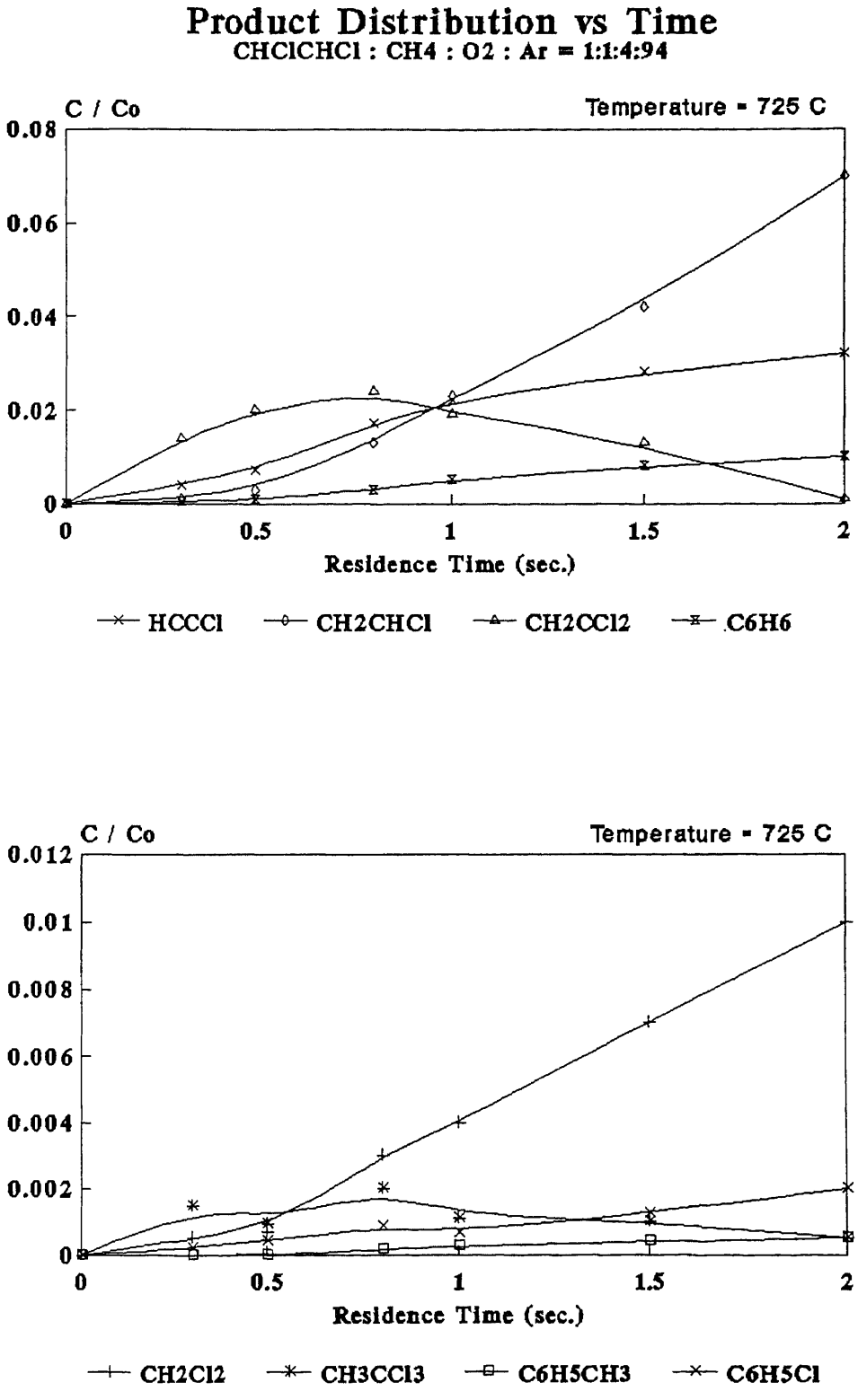

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:4:94
C / Co
Temperature = 725 C
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Temperature = 725 C
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.32

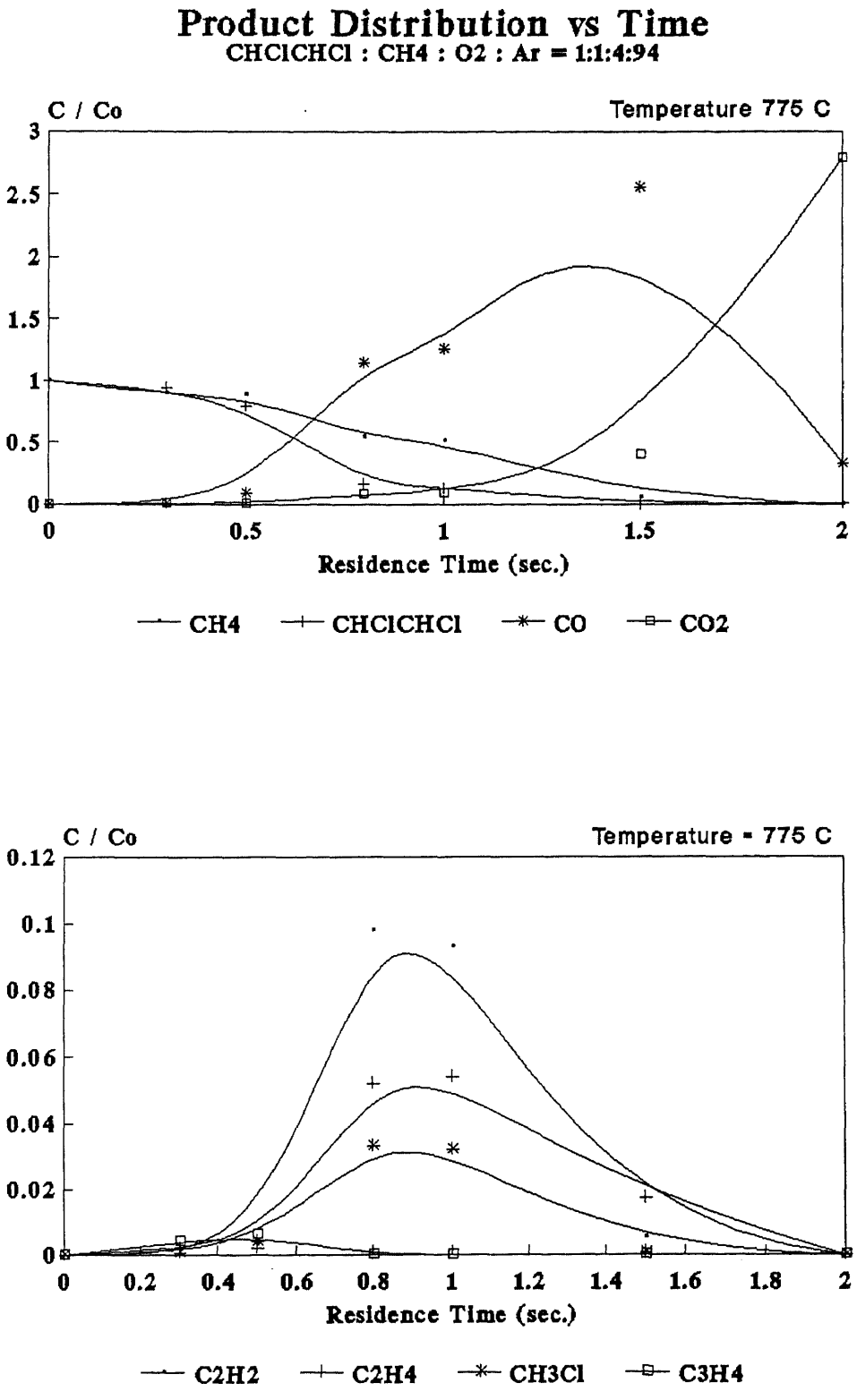

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:4:94
C / Co
Temperature 775 C
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
CHClCHCl
CO
CO2
C / Co
Temperature = 775 C
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.33

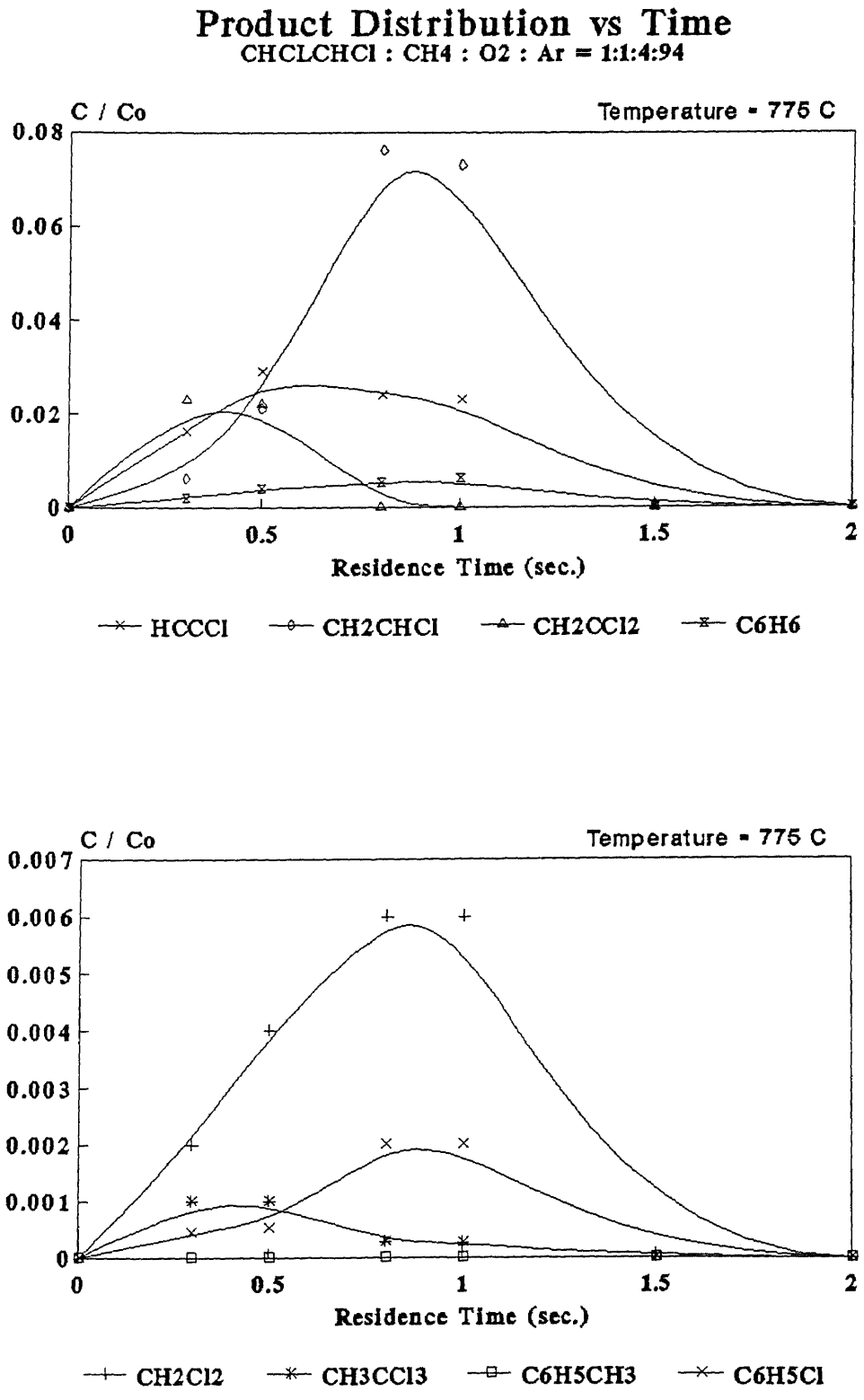

Product Distribution vs Time
CHCLCHCl : CH4 : O2 : Ar = 1:1:4:94
C / Co
Temperature = 775 C
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Temperature = 775 C
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.34

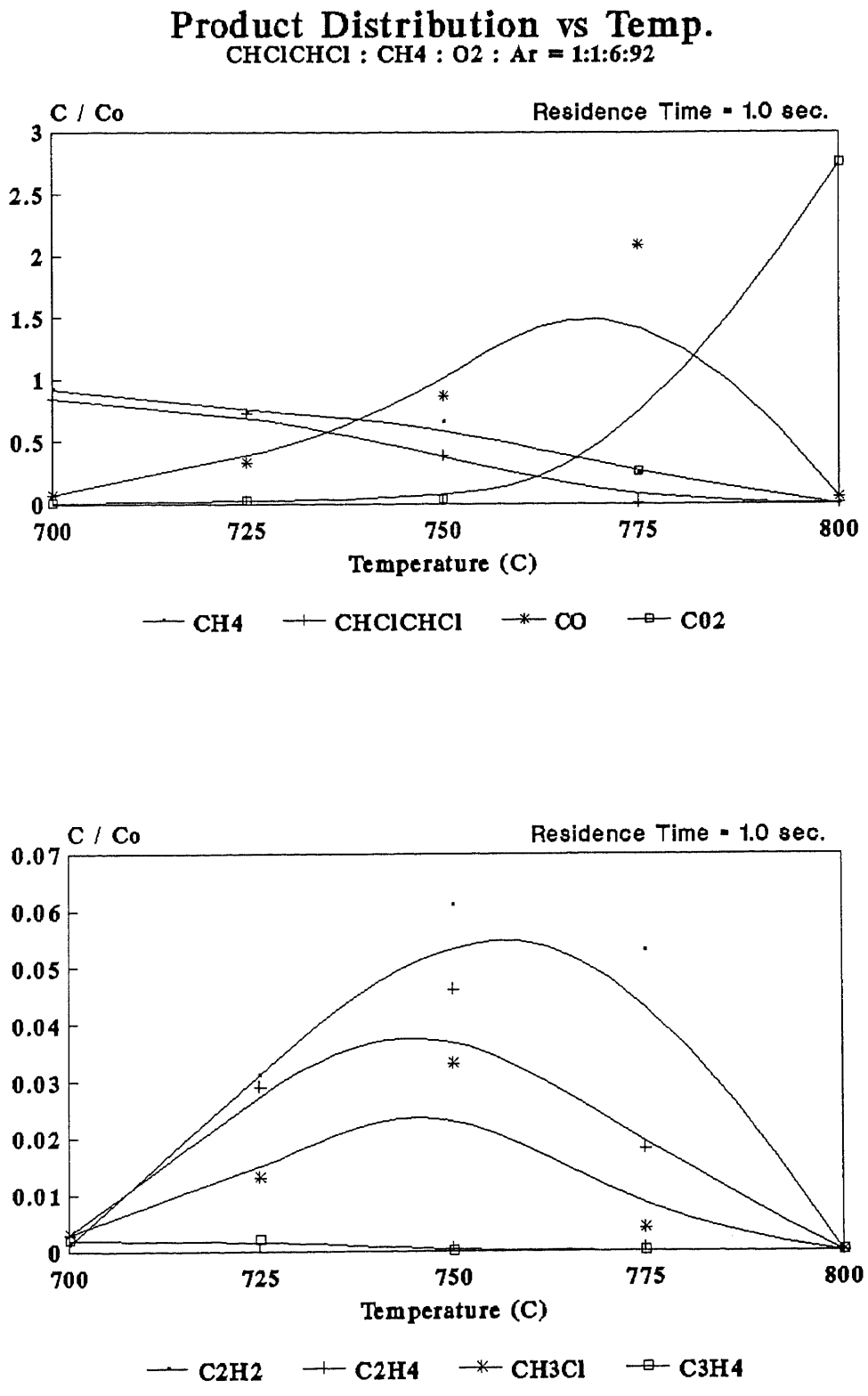

Product Distribution vs Temp.
CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Residence Time = 1.0 sec.
3
2.5
2
1.5
1
0.5
0
700
725
750
775
800
Temperature (C)
CH4
CHClCHCl
CO
C02
C / Co
Residence Time = 1.0 sec.
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
700
725
750
775
800
Temperature (C)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.35

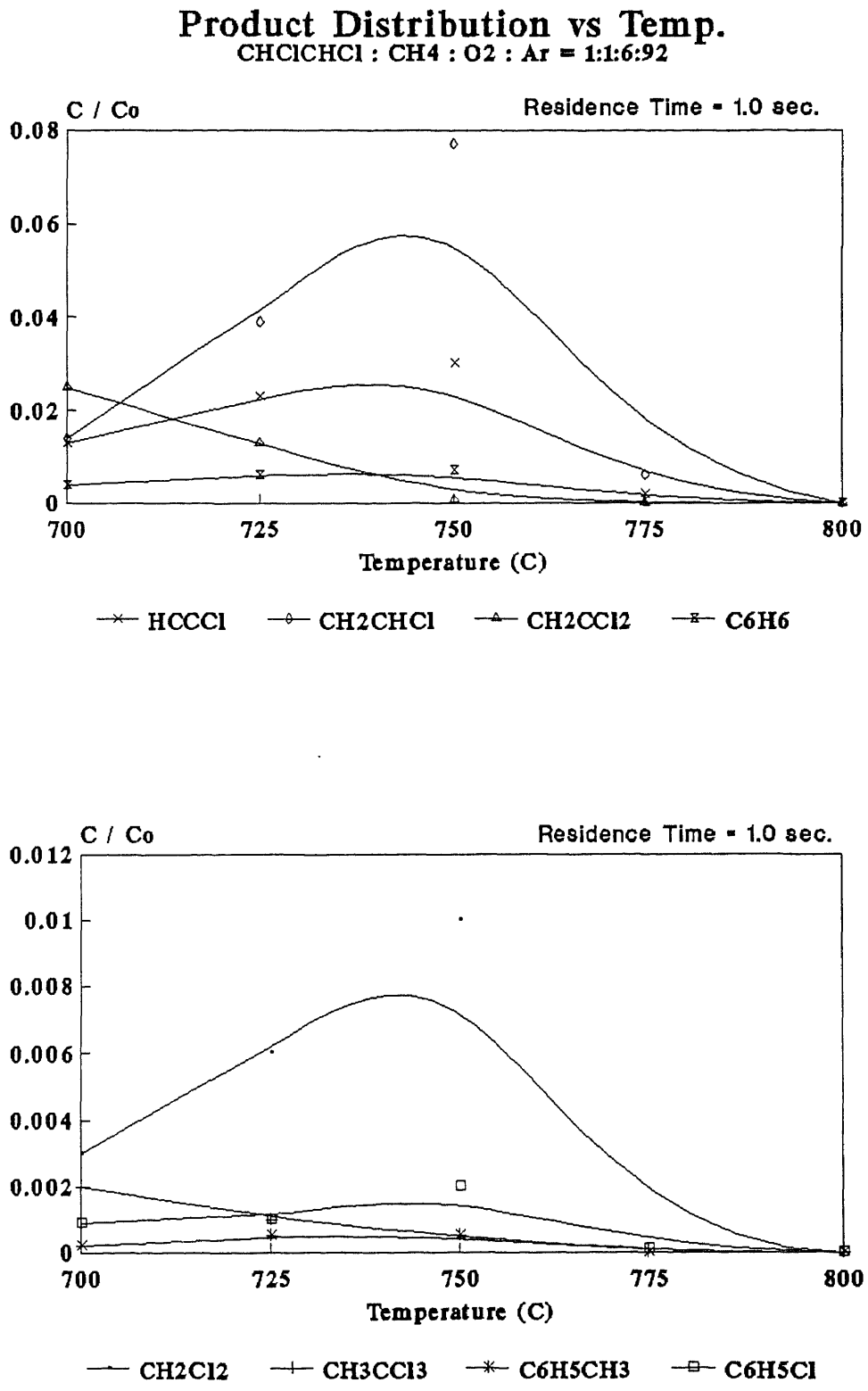

Product Distribution vs Temp.
CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Residence Time = 1.0 sec.
0.08
0.06
0.04
0.02
0
700
725
750
775
800
Temperature (C)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Residence Time = 1.0 sec.
0.012
0.01
0.008
0.006
0.004
0.002
0
700
725
750
775
800
Temperature (C)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.36

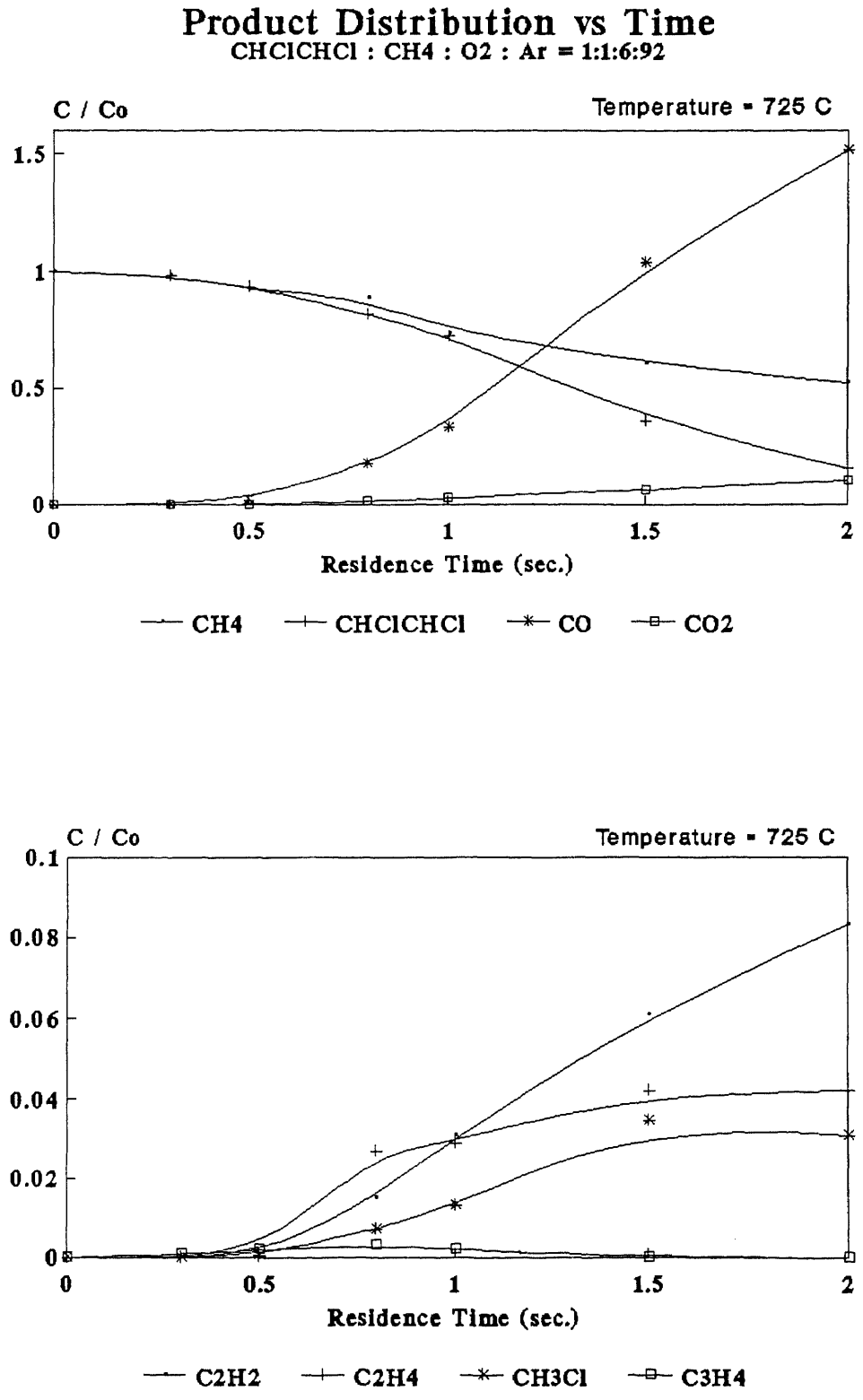

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
CHClCHCl
CO
CO2
C / Co
Temperature = 725 C
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.37

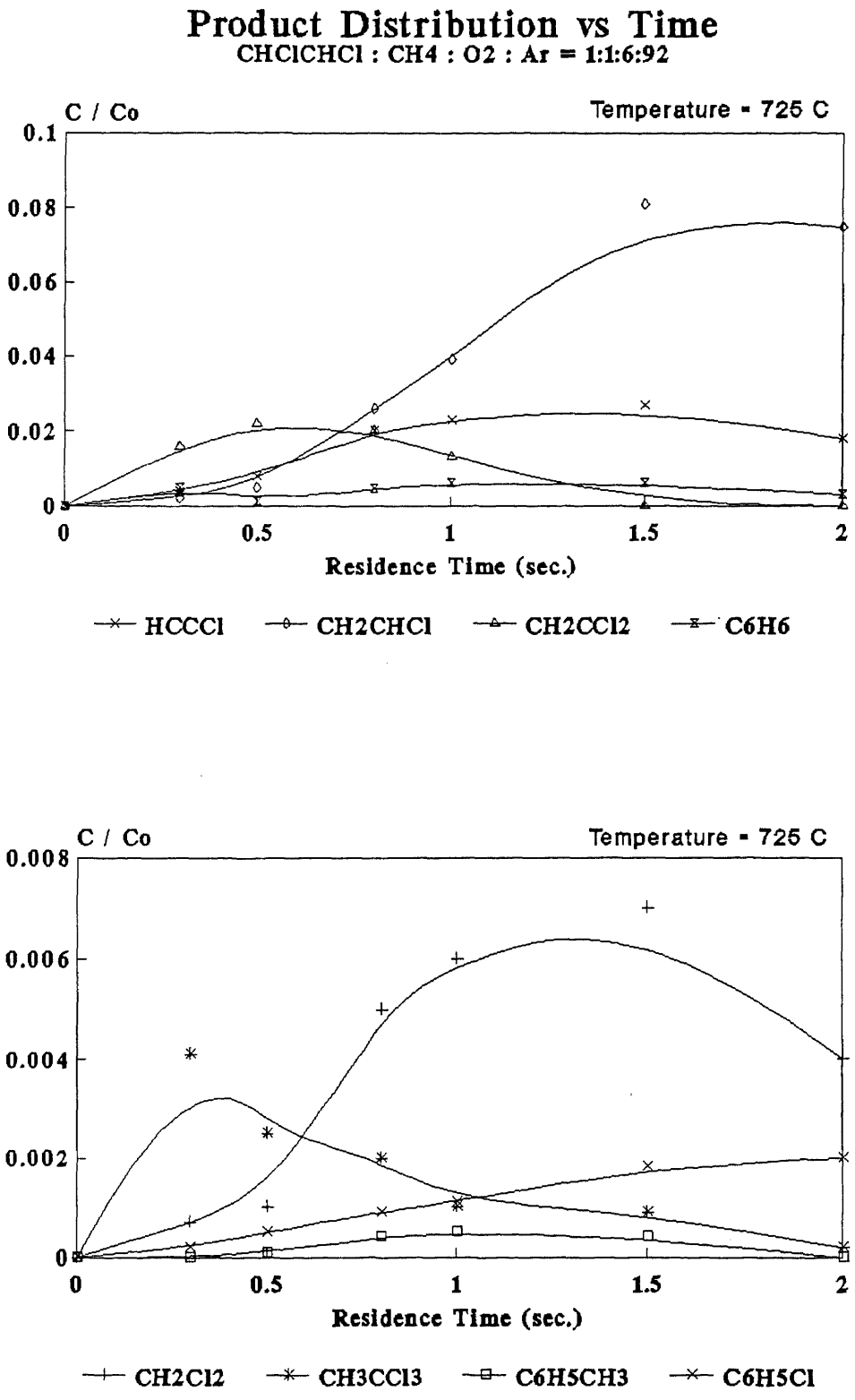

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Temperature = 725 C
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.38

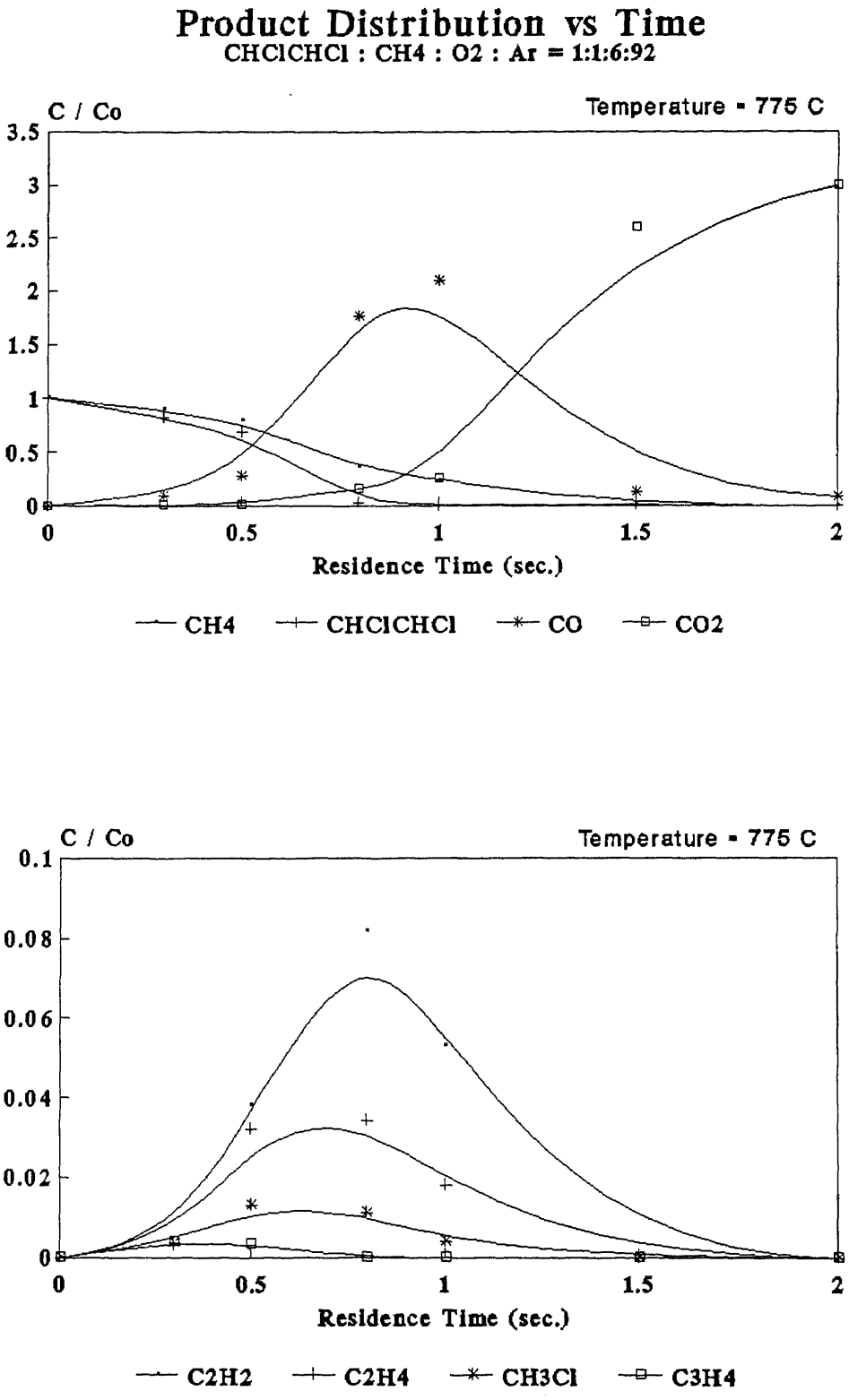

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 775 C
3.5
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
CHClCHCl
CO
CO2
C / Co
Temperature = 775 C
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.39

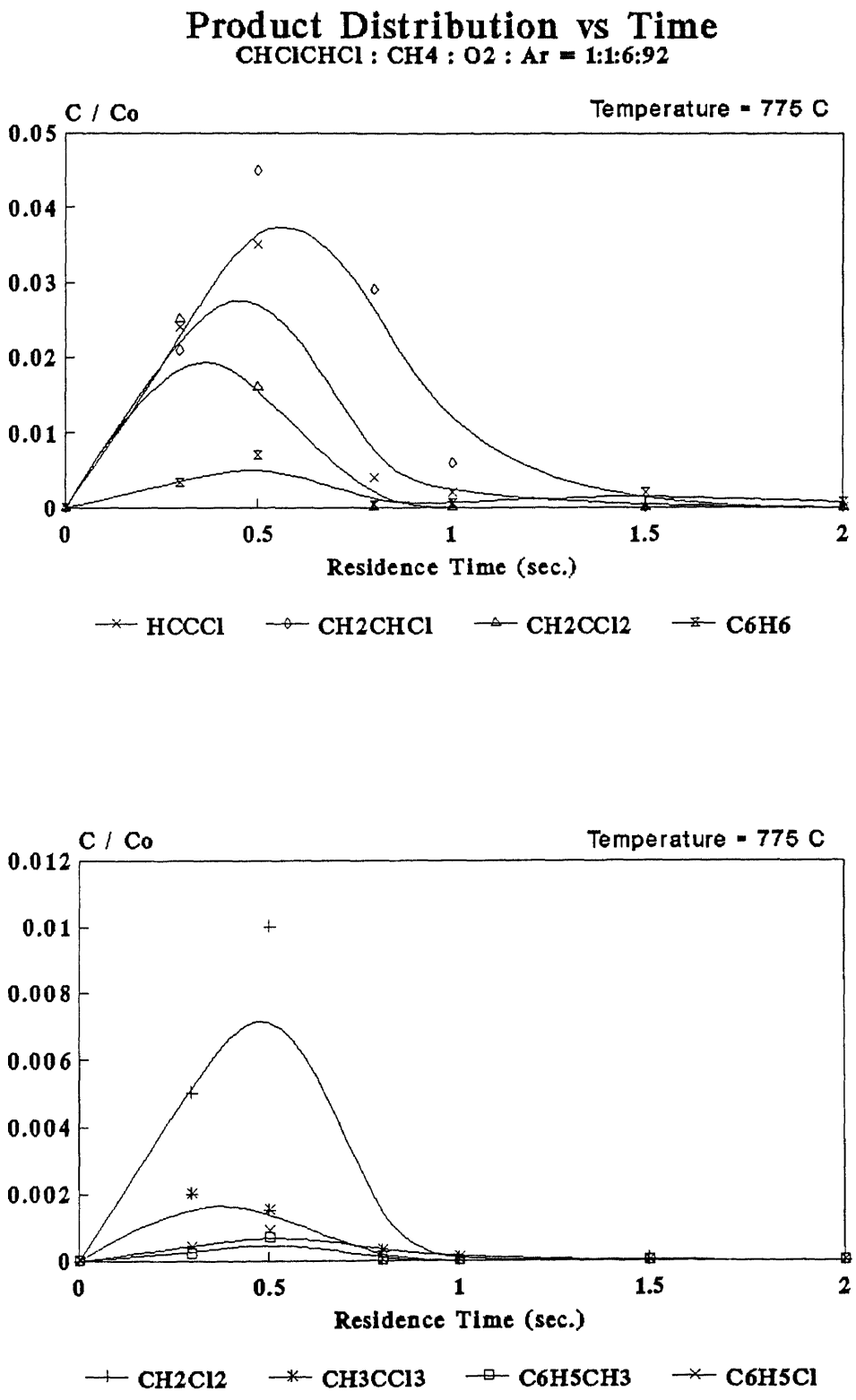

Product Distribution vs Time
CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 775 C
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6
C / Co
Temperature = 775 C
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.40

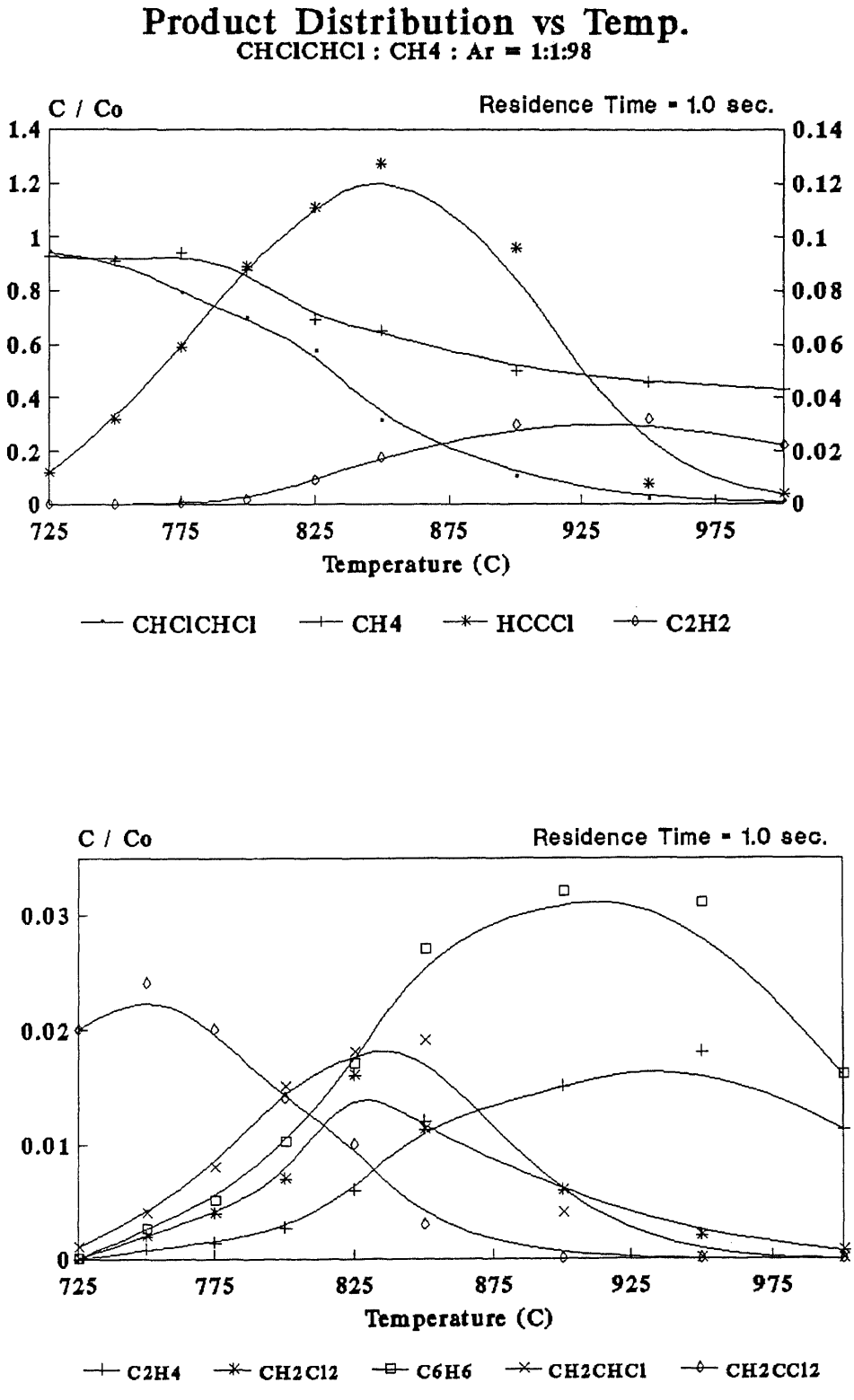

Product Distribution vs Temp.
CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Residence Time = 1.0 sec.
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
725
775
825
875
925
975
Temperature (C)
CHClCHCl
CH4
HCCCl
C2H2
C / Co
Residence Time = 1.0 sec.
0.03
0.02
0.01
0
725
775
825
875
925
975
Temperature (C)
C2H4
CH2Cl2
C6H6
CH2CHCl
CH2CCl2

Figure 4.41

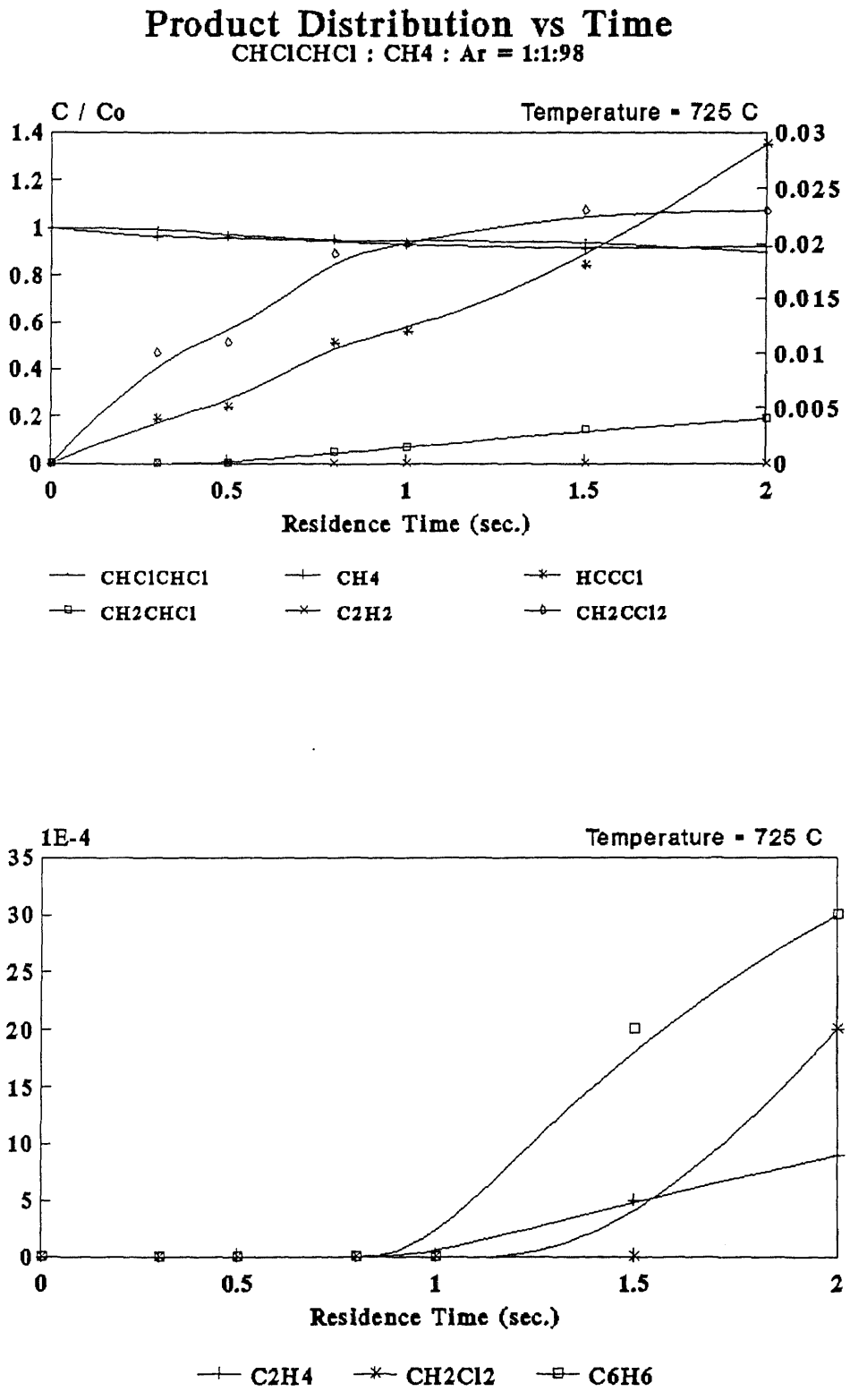
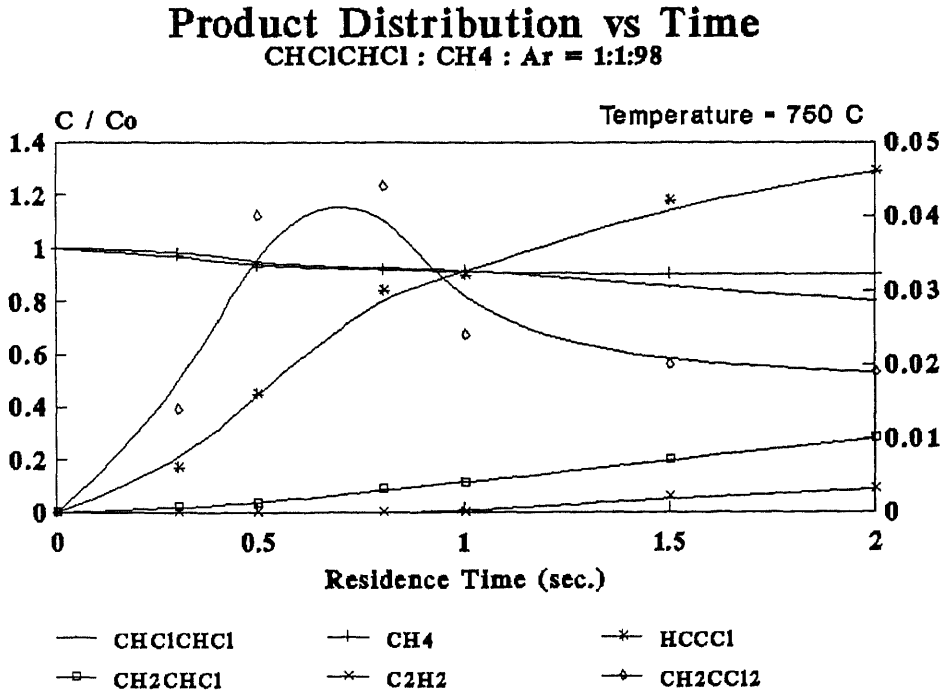

Product Distribution vs Time
CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Temperature = 725 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CH4
HCCCl
CH2CHCl
C2H2
CH2CCl2
1E-4
Temperature = 725 C
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H4
CH2Cl2
C6H6

Figure 4.42


Product Distribution vs Time
CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Temperature = 750 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CH4
HCCCl
CH2CHCl
C2H2
CH2CCl2

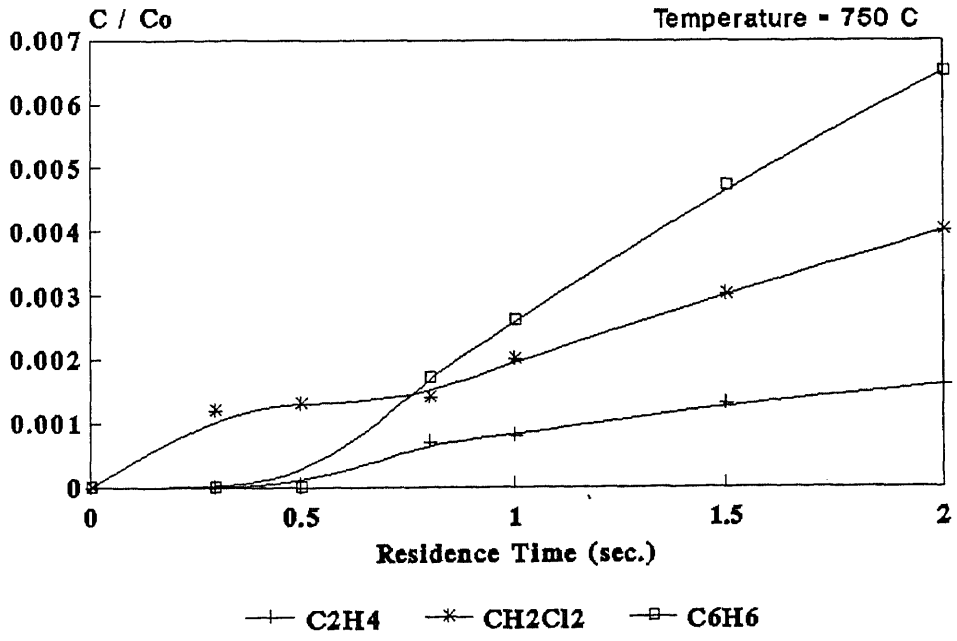
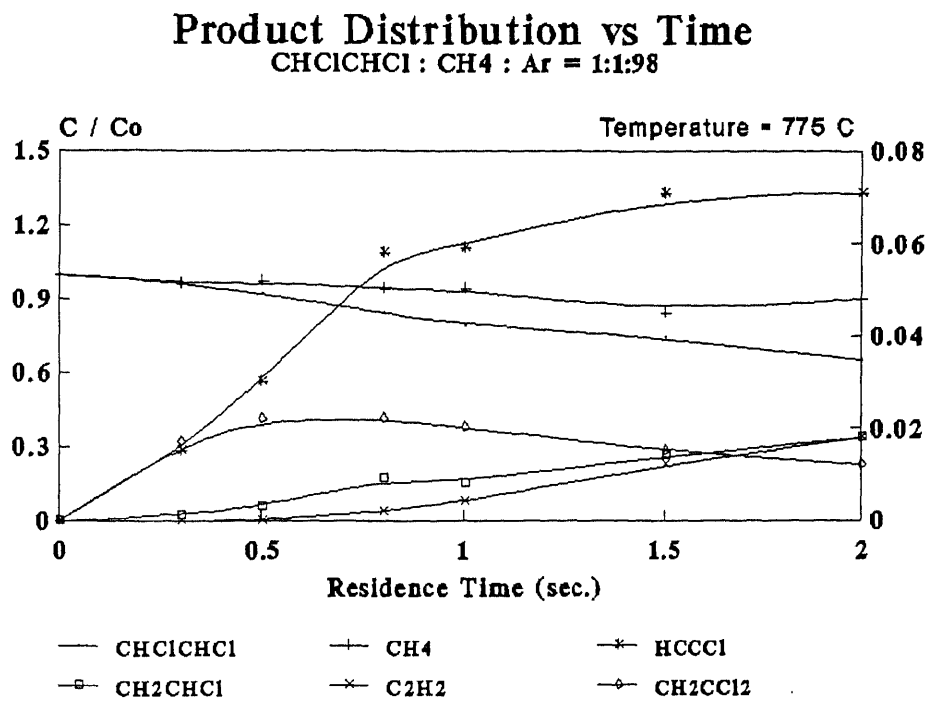

C / Co
Temperature = 750 C
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H4
CH2Cl2
C6H6

Figure 4.43


Product Distribution vs Time
CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Temperature = 775 C
1.5
1.2
0.9
0.6
0.3
0
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CH4
HCCCl
CH2CHCl
C2H2
CH2CCl2

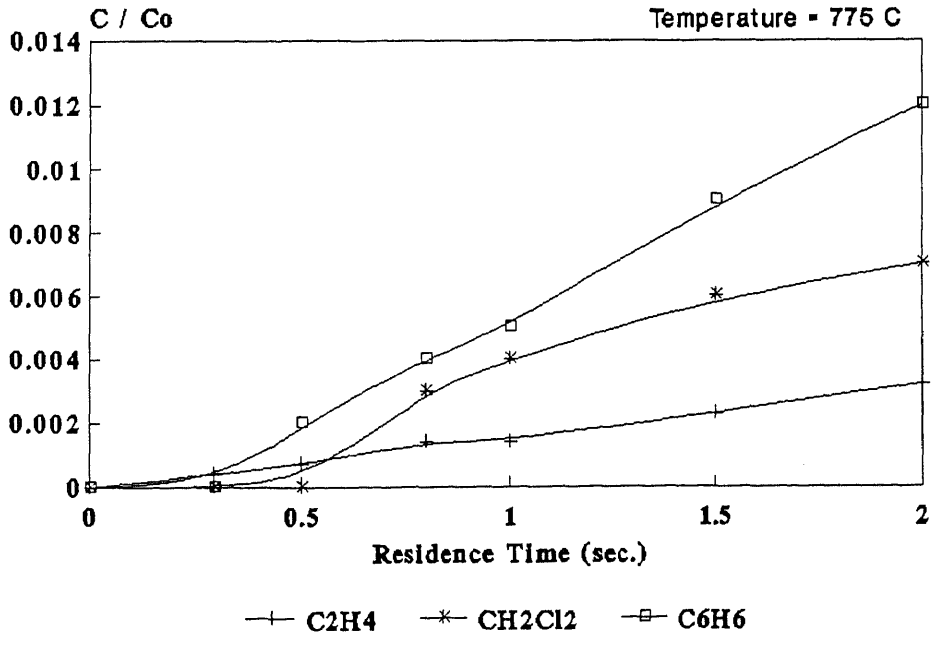

C / Co
Temperature = 775 C
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H4
CH2Cl2
C6H6

Figure 4.44

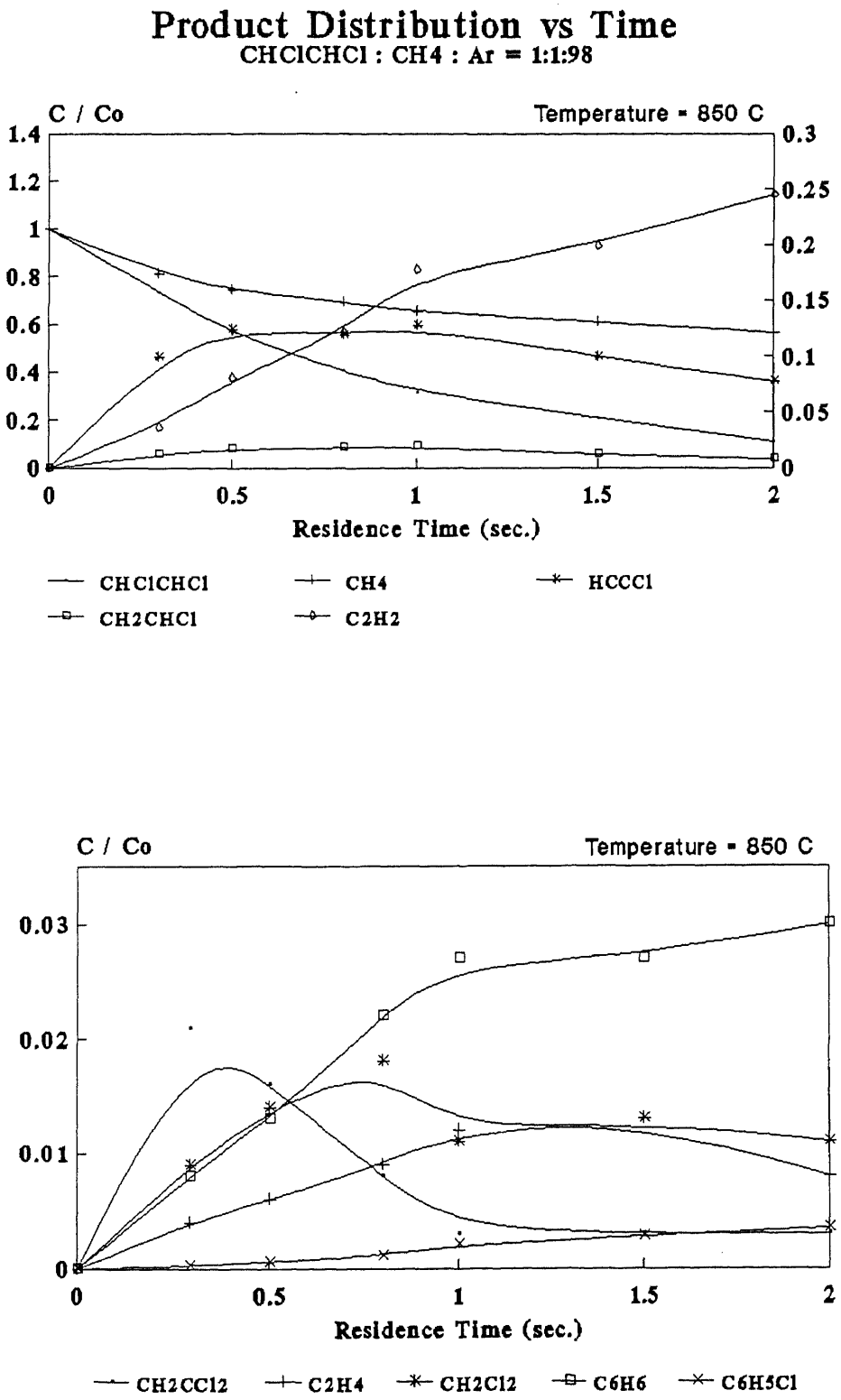

Product Distribution vs Time
CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Temperature = 850 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CH4
HCCCl
CH2CHCl
C2H2
C / Co
Temperature = 850 C
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2CCl2
C2H4
CH2Cl2
C6H6
C6H5Cl

Figure 4.45

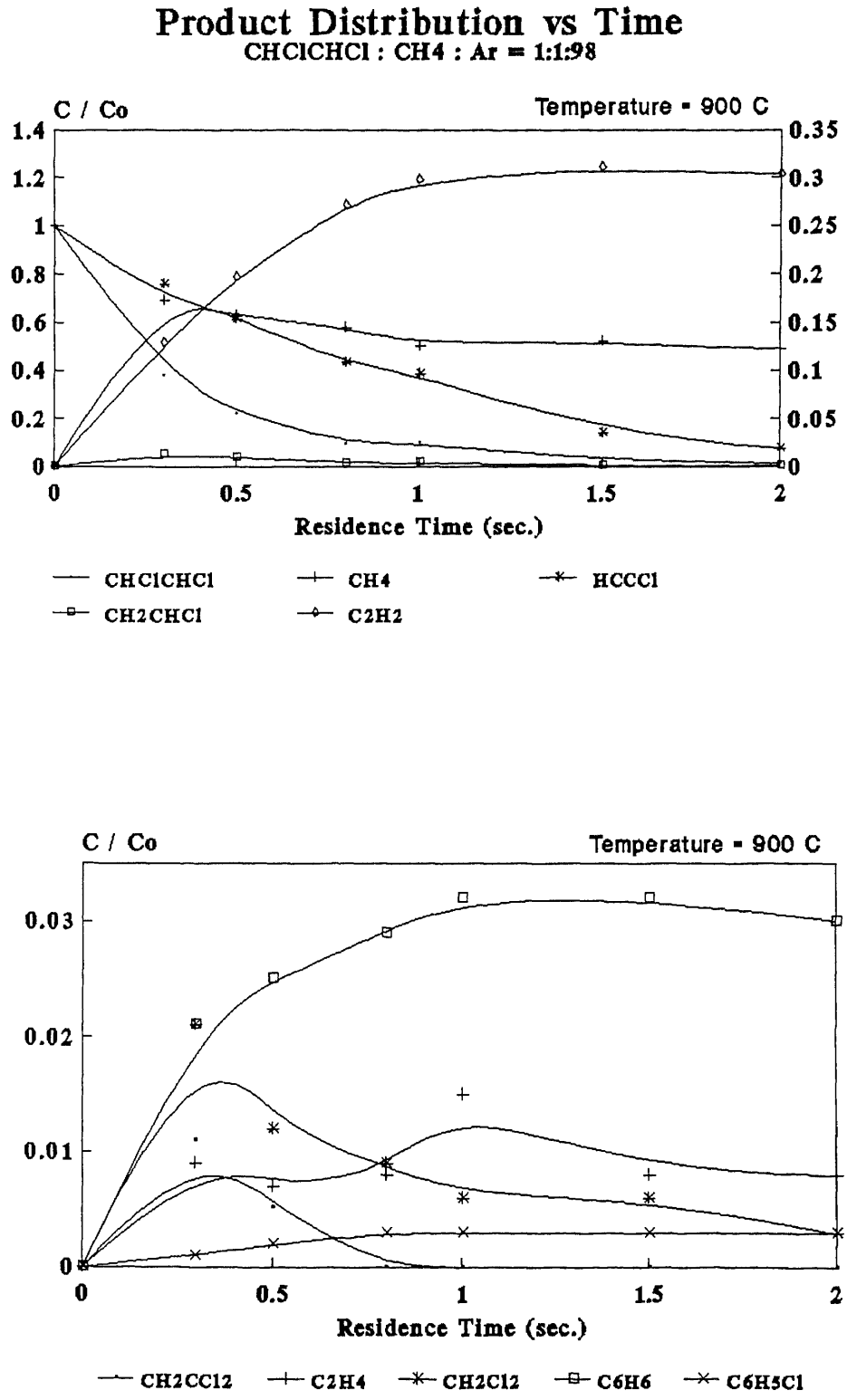

Product Distribution vs Time
CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Temperature = 900 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CH4
HCCCl
CH2CHCl
C2H2
C / Co
Temperature = 900 C
0.03
0.02
0.01
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2CCl2
C2H4
CH2Cl2
C6H6
C6H5Cl

Figure 4.46

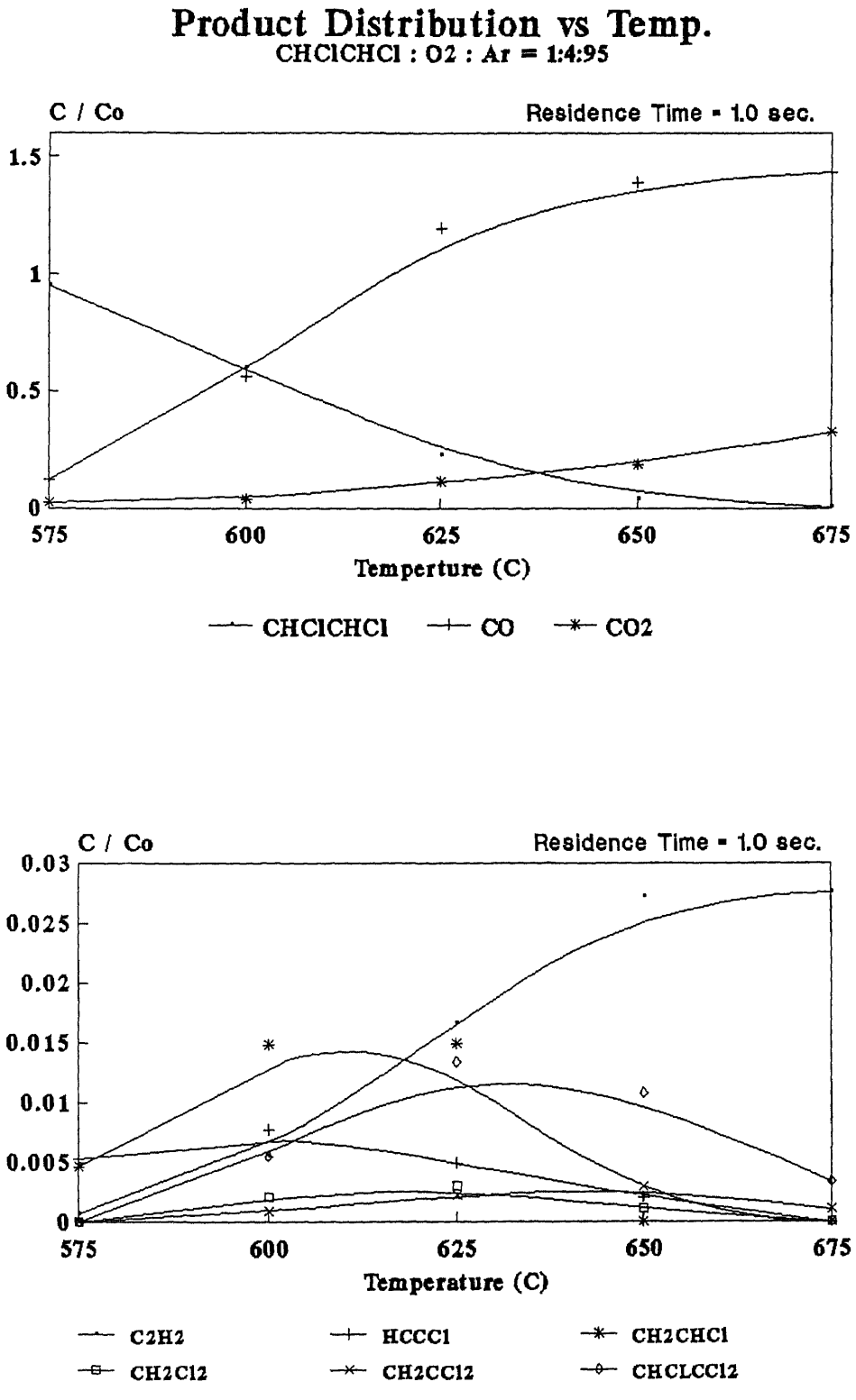

Product Distribution vs Temp.
CHClCHCl : O2 : Ar = 1:4:95
C / Co
Residence Time = 1.0 sec.
1.5
1
0.5
0
575
600
625
650
675
Temperture (C)
CHClCHCl
CO
CO2
C / Co
Residence Time = 1.0 sec.
0.03
0.025
0.02
0.015
0.01
0.005
0
575
600
625
650
675
Temperature (C)
C2H2
HCCCl
CH2CHCl
CH2Cl2
CH2CCl2
CHCLCCl2

Figure 4.47

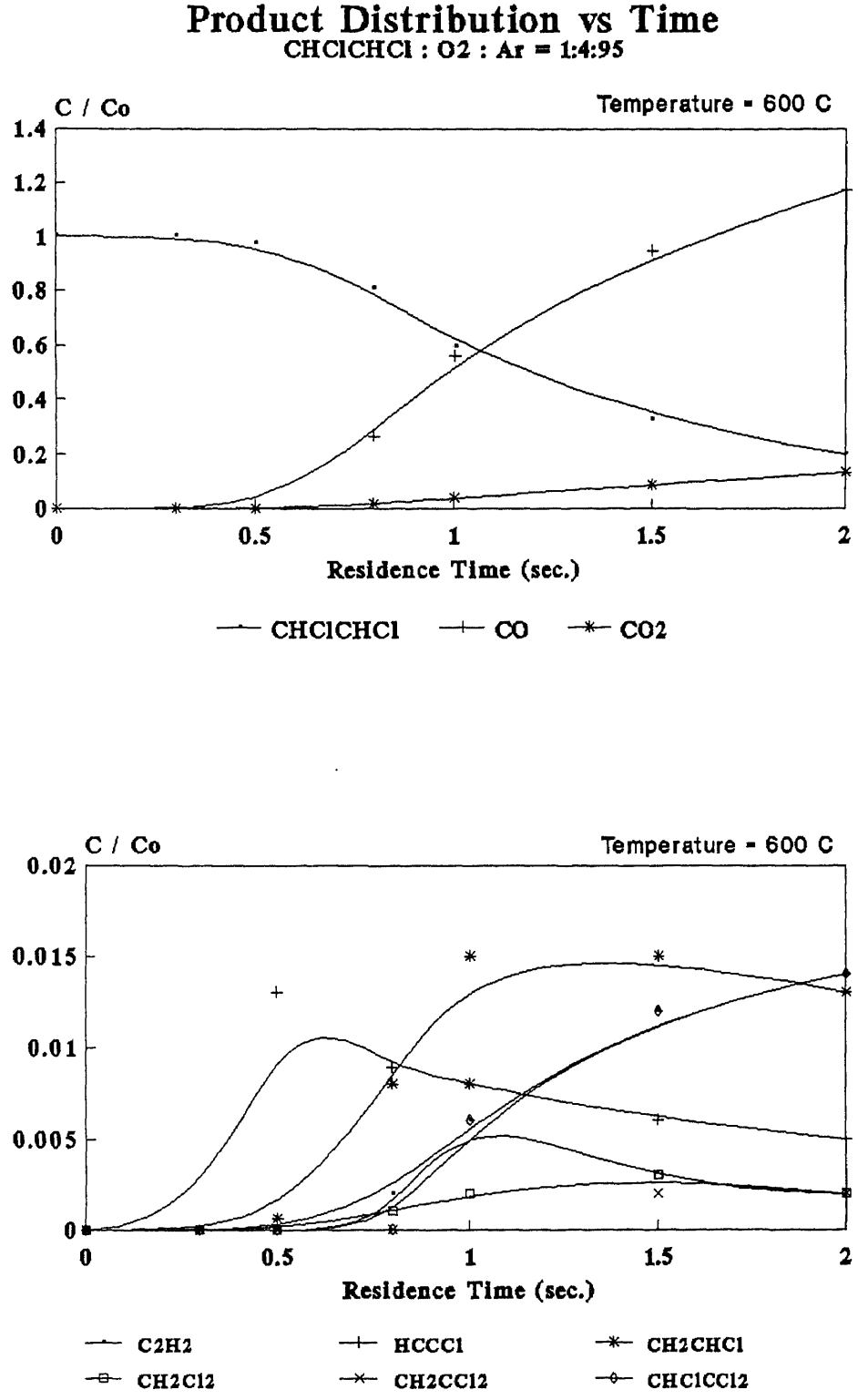

Product Distribution vs Time
CHClCHCl : O2 : Ar = 1:4:95
C / Co
Temperature = 600 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CO
CO2
C / Co
Temperature = 600 C
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
HCCCl
CH2CHCl
CH2Cl2
CH2CCl2
CHClCCl2

Figure 4.48

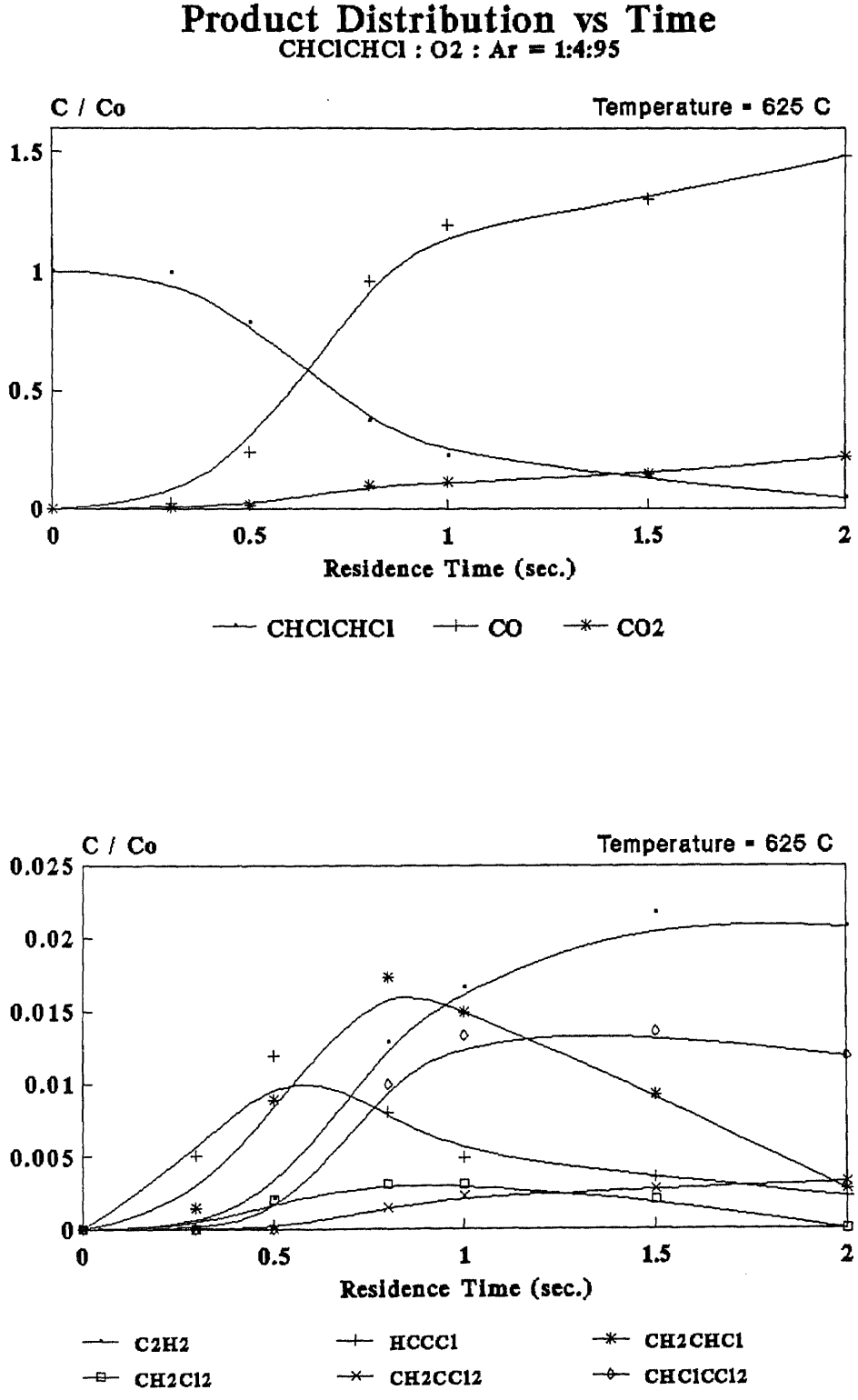

Product Distribution vs Time
CHClCHCl : O2 : Ar = 1:4:95
C / Co
Temperature = 625 C
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CO
CO2
C / Co
Temperature = 625 C
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
HCCCl
CH2CHCl
CH2Cl2
CH2CCl2
CHClCCl2

Figure 4.49

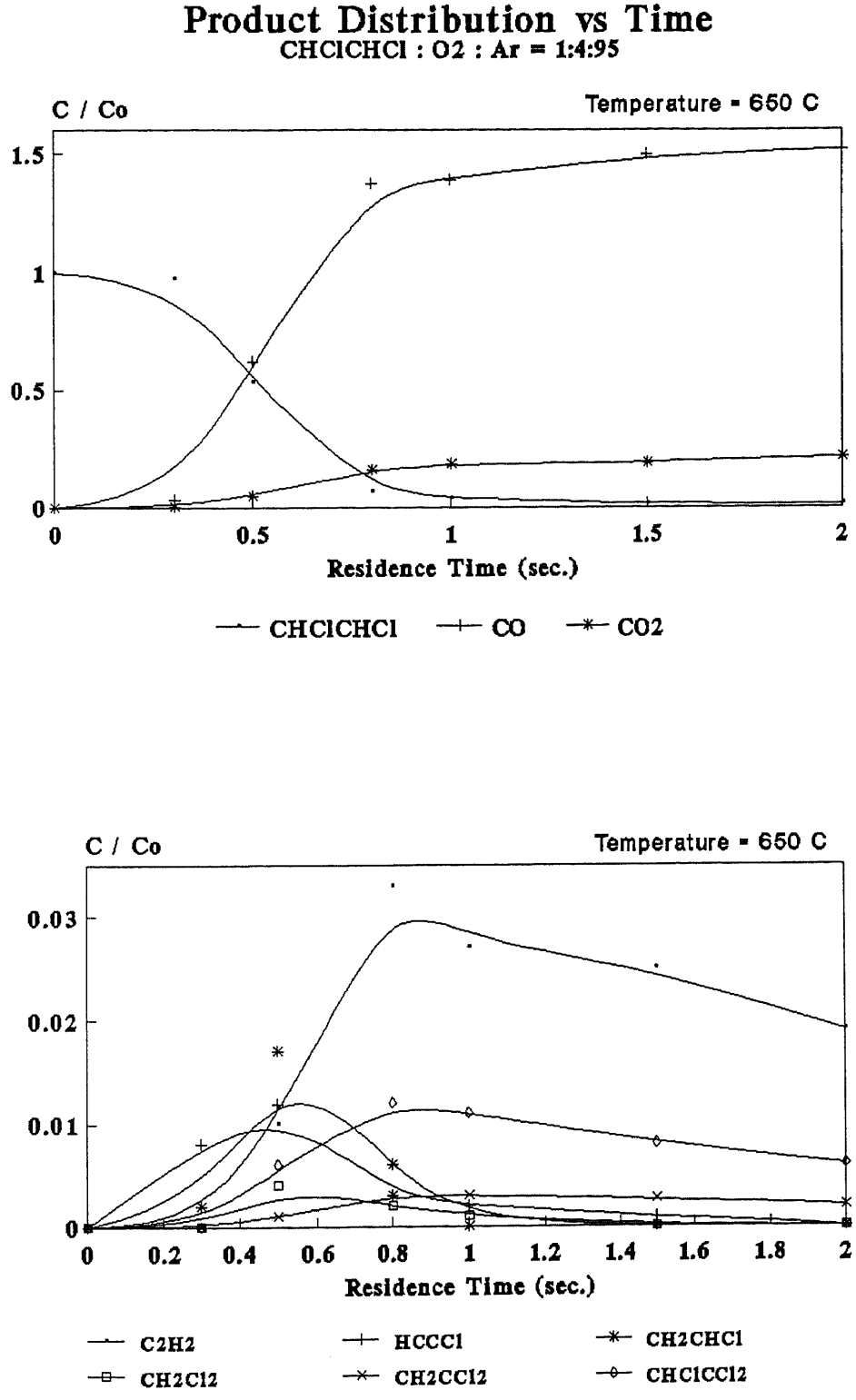
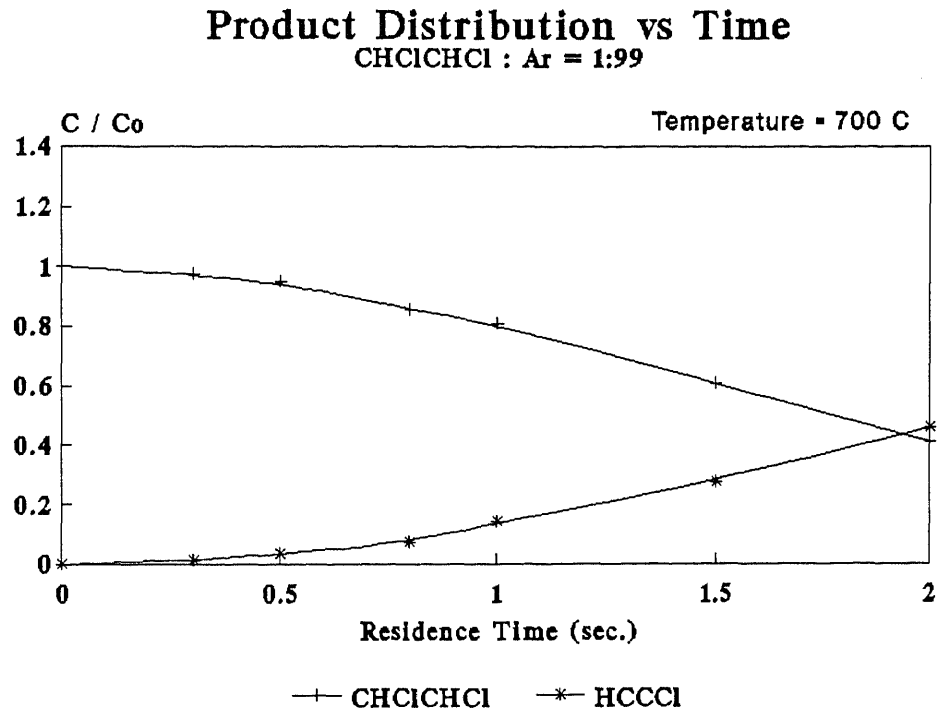

Product Distribution vs Time
CHClCHCl : O2 : Ar = 1:4:95
C / Co
Temperature = 650 C
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
CO
CO2
C / Co
Temperature = 650 C
0.03
0.02
0.01
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Residence Time (sec.)
C2H2
HCCCl
CH2CHCl
CH2Cl2
CH2CCl2
CHClCCl2

Figure 4.50


Product Distribution vs Time
CHClCHCl : Ar = 1:99
C / Co
Temperature = 700 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
HCCCl

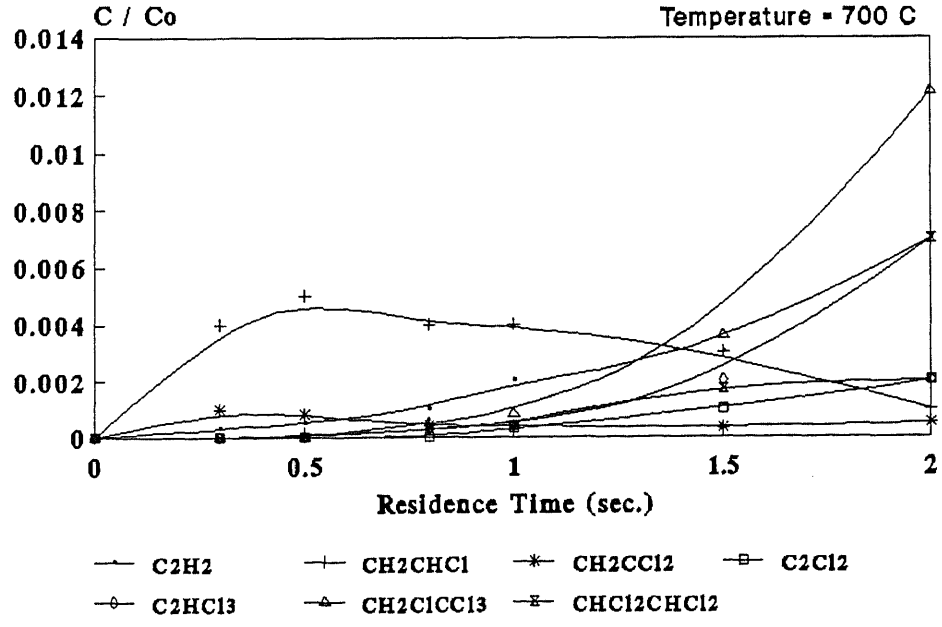
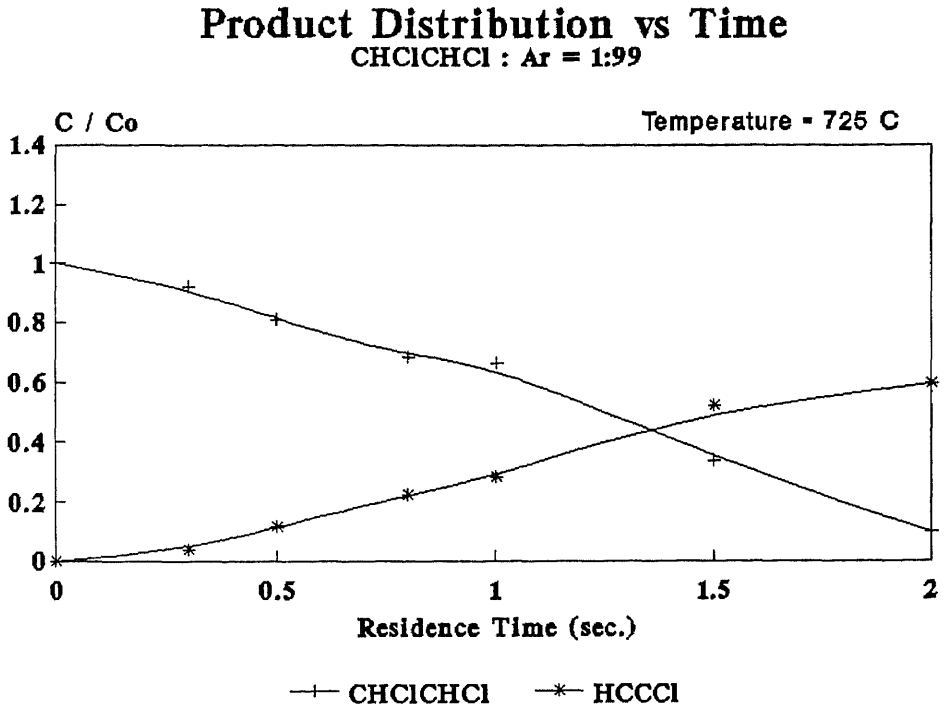

C / Co
Temperature = 700 C
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
CH2CHCl
CH2CCl2
C2Cl2
C2HCl3
CH2ClCCl3
CHCl2CHCl2

Figure 4.51


Product Distribution vs Time
CHClCHCl : Ar = 1:99
C / Co
Temperature = 725 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
Residence Time (sec.)
CHClCHCl
HCCCl

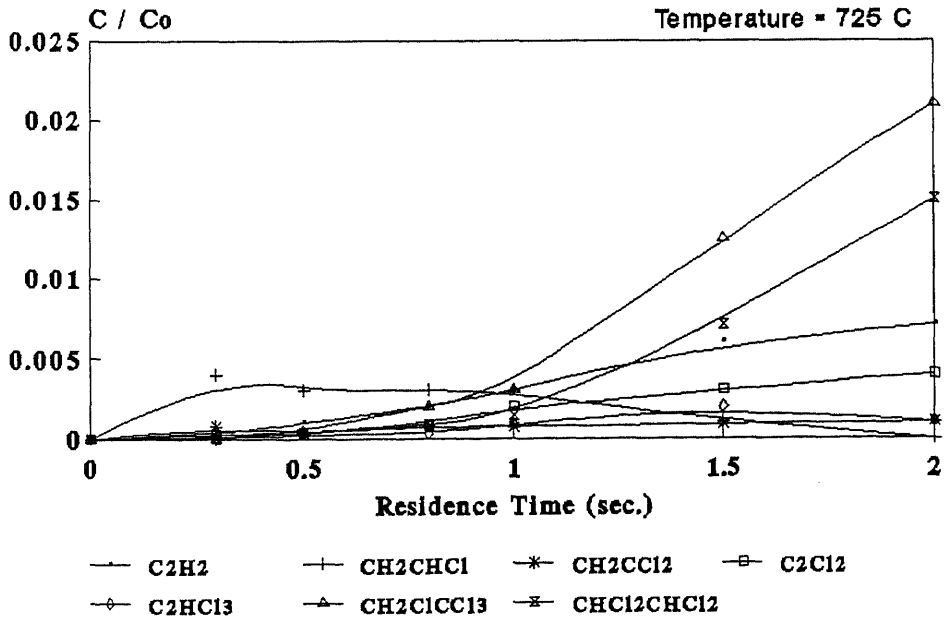

C / Co
Temperature = 725 C
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
CH2CHCl
CH2CCl2
C2Cl2
C2HCl3
CH2ClCCl3
CHCl2CHCl2

Figure 4.52

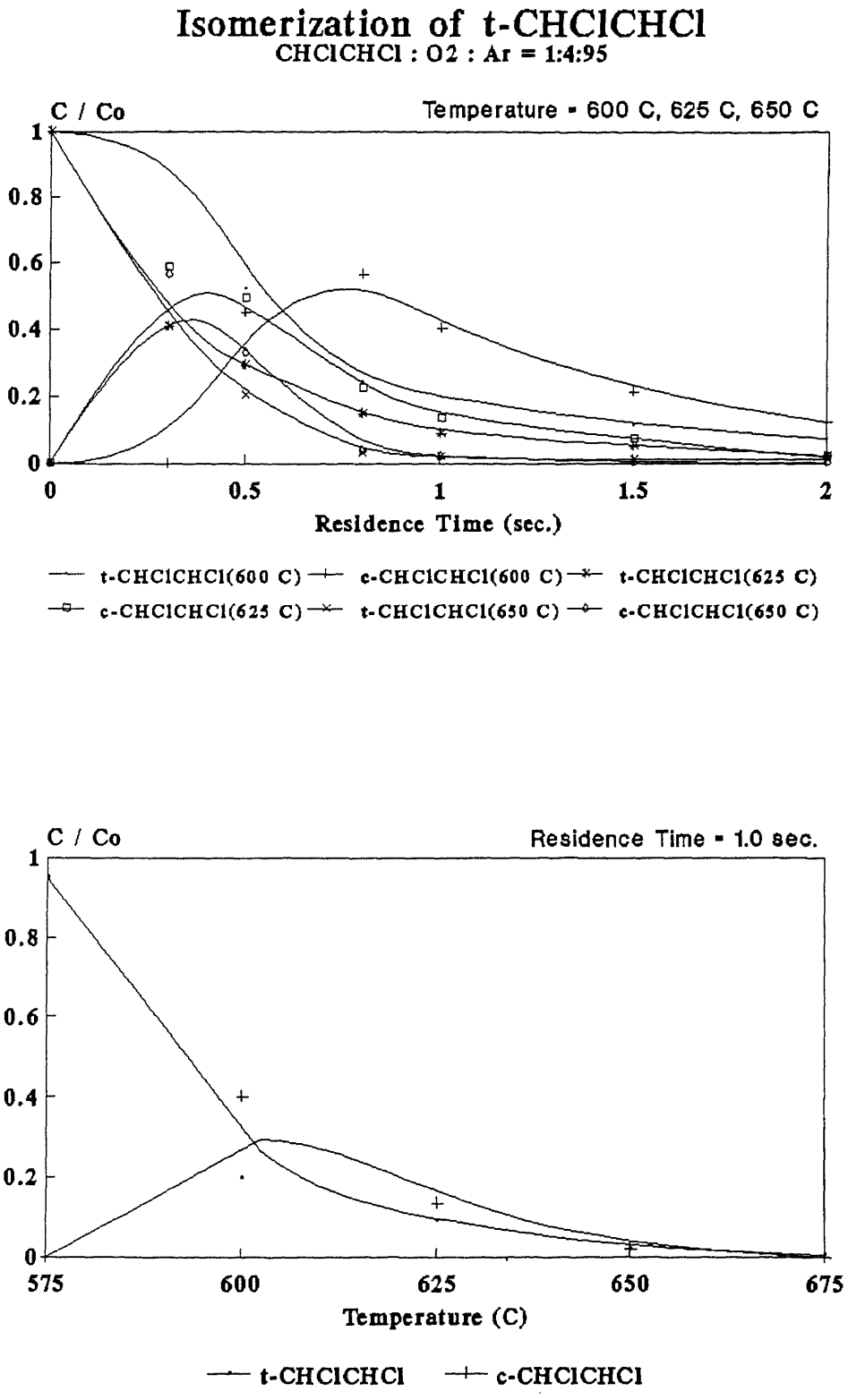

Isomerization of t-CHClCHCl
CHClCHCl : O2 : Ar = 1:4:95
C / Co
Temperature = 600 C, 625 C, 650 C
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
Residence Time (sec.)
t-CHClCHCl(600 C)
c-CHClCHCl(600 C)
t-CHClCHCl(625 C)
c-CHClCHCl(625 C)
t-CHClCHCl(650 C)
c-CHClCHCl(650 C)
C / Co
Residence Time = 1.0 sec.
1
0.8
0.6
0.4
0.2
0
575
600
625
650
675
Temperature (C)
t-CHClCHCl
c-CHClCHCl

Figure 4.53

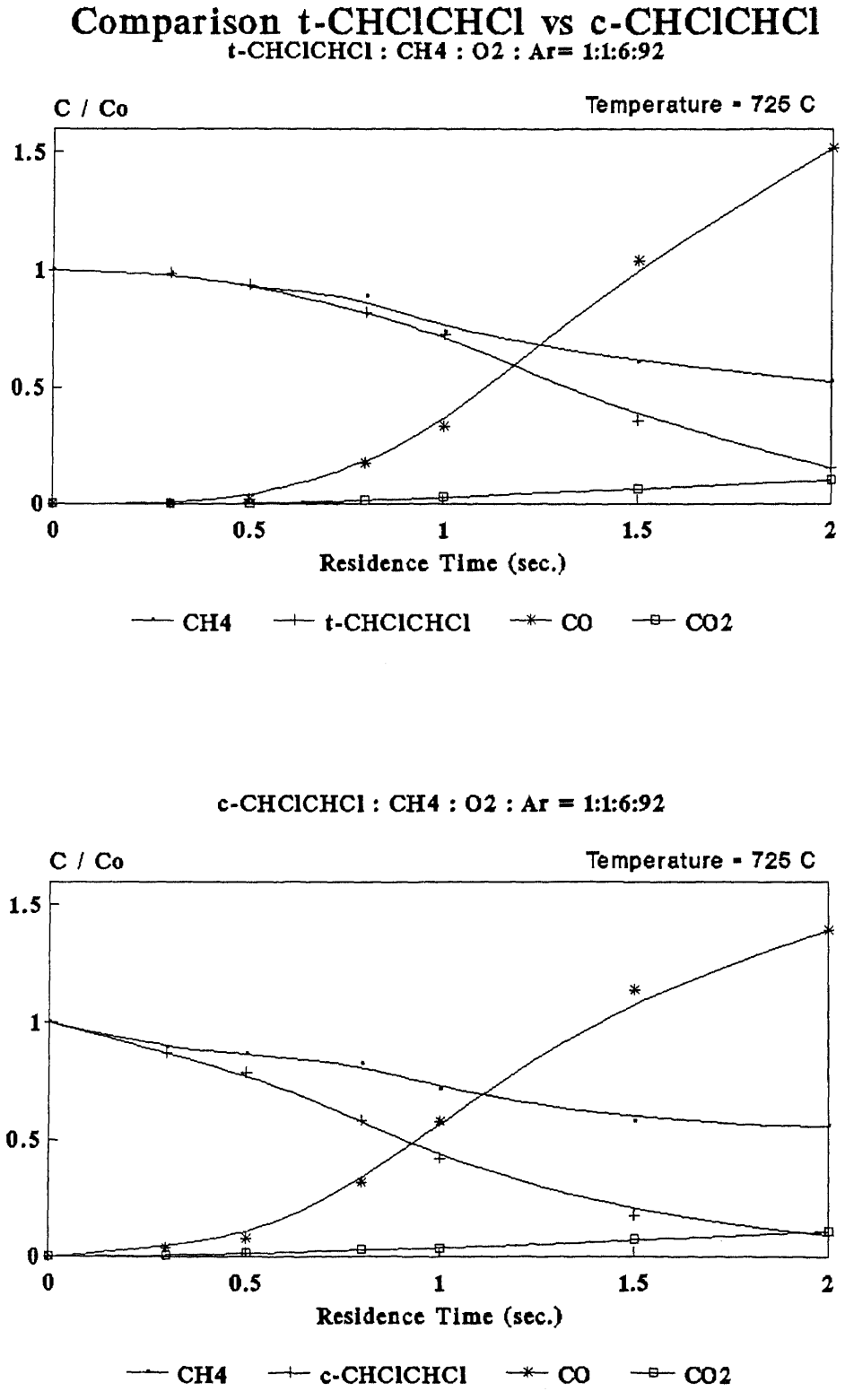

Comparison t-CHClCHCl vs c-CHClCHCl
t-CHClCHCl : CH4 : O2 : Ar= 1:1:6:92
C / Co
Temperature = 725 C
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
t-CHClCHCl
CO
CO2
c-CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
1.5
1
0.5
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH4
c-CHClCHCl
CO
CO2

Figure 4.54

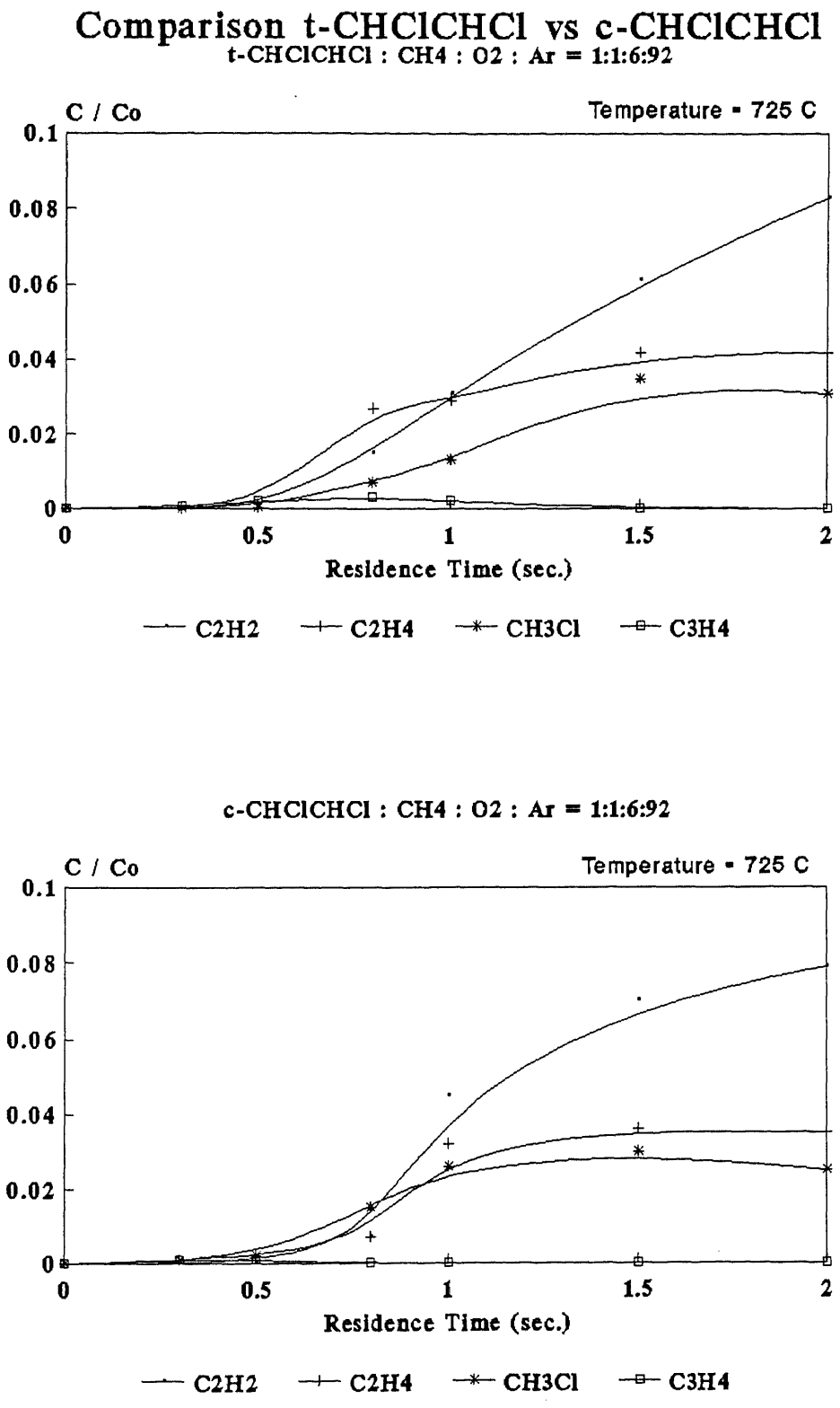

Comparison t-CHClCHCl vs c-CHClCHCl
t-CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4
c-CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH3Cl
C3H4

Figure 4.55

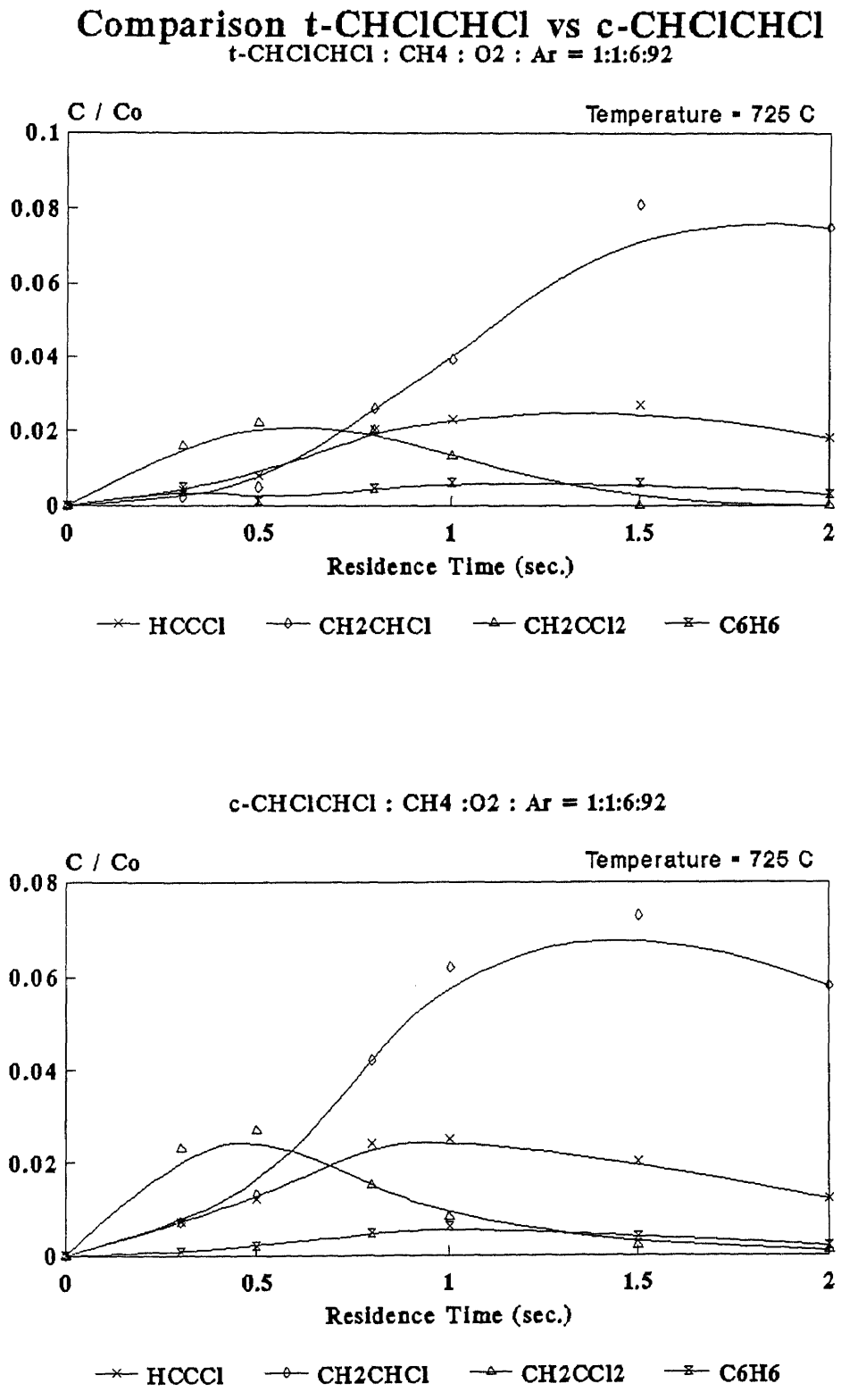

Comparison t-CHClCHCl vs c-CHClCHCl
t-CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6
c-CHClCHCl : CH4 :O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
Residence Time (sec.)
HCCCl
CH2CHCl
CH2CCl2
C6H6

Figure 4.56

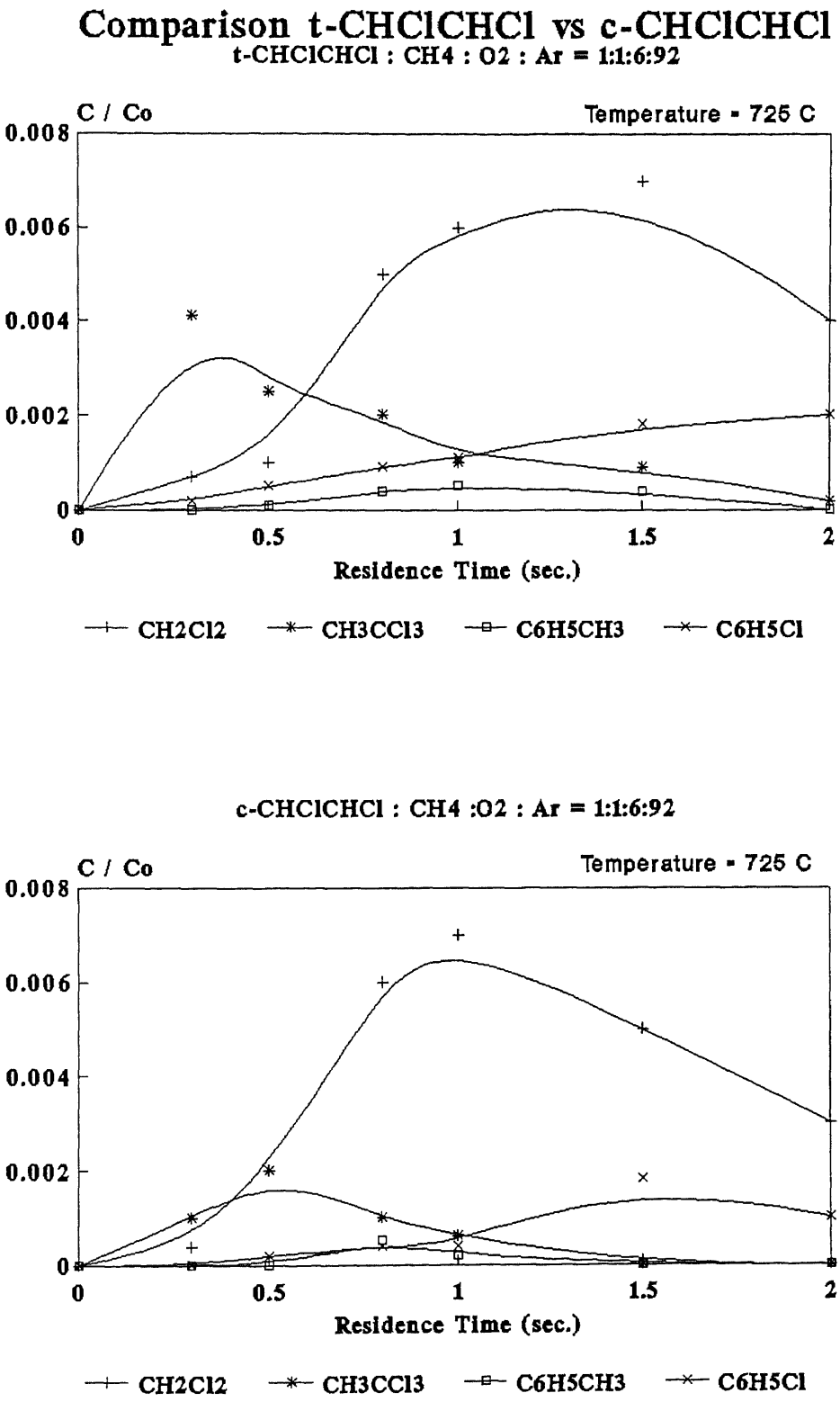

Comparison t-CHClCHCl vs c-CHClCHCl
t-CHClCHCl : CH4 : O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl
c-CHClCHCl : CH4 :O2 : Ar = 1:1:6:92
C / Co
Temperature = 725 C
0.008
0.006
0.004
0.002
0
0
0.5
1
1.5
2
Residence Time (sec.)
CH2Cl2
CH3CCl3
C6H5CH3
C6H5Cl

Figure 4.57

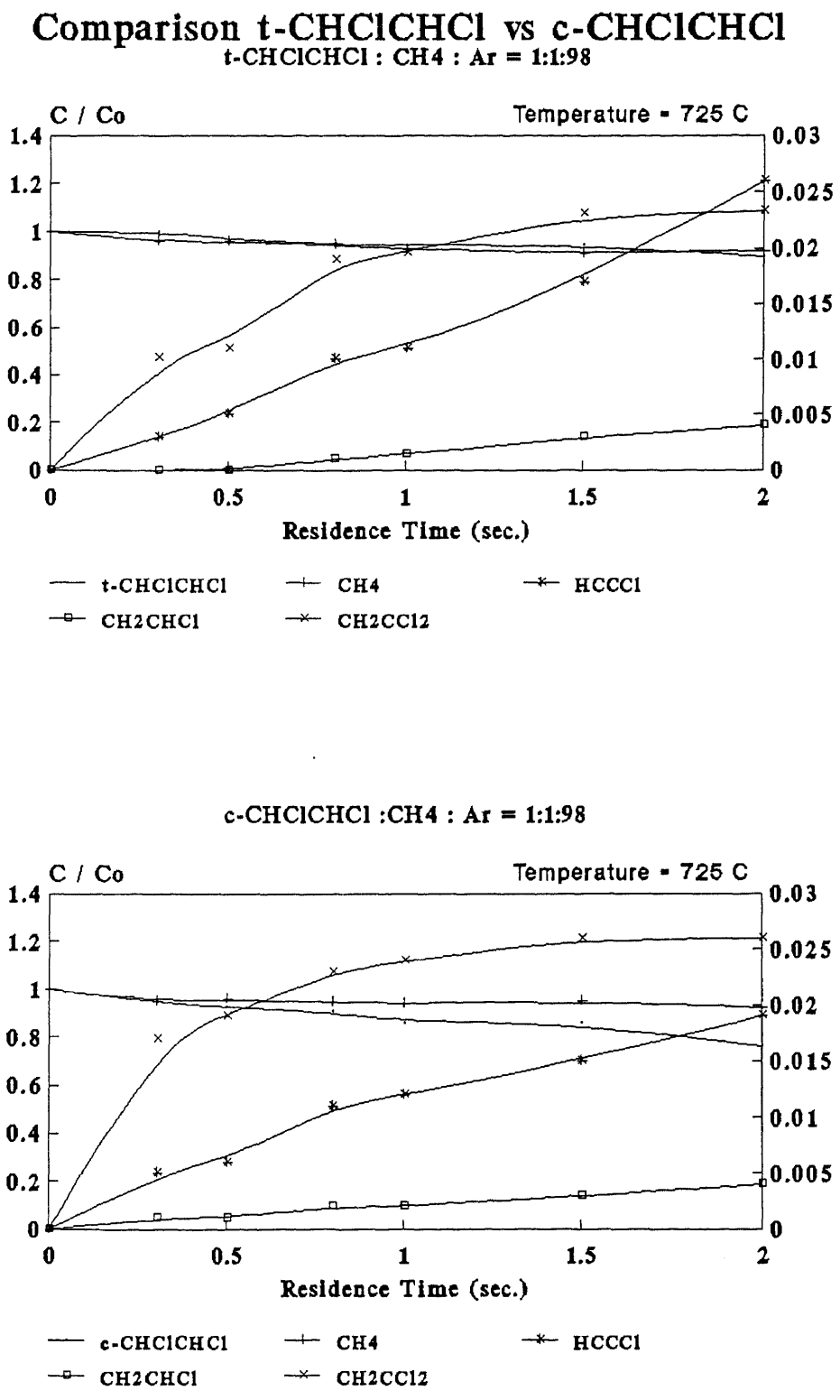

Comparison t-CHClCHCl vs c-CHClCHCl
t-CHClCHCl : CH4 : Ar = 1:1:98
C / Co
Temperature = 725 C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
Residence Time (sec.)
t-CHClCHCl
CH4
HCCCl
CH2CHCl
CH2CCl2
c-CHClCHCl :CH4 : Ar = 1:1:98
C / Co
Temperature = 725 C
Residence Time (sec.)
c-CHClCHCl
CH4
HCCCl
CH2CHCl
CH2CCl2

Figure 4.58

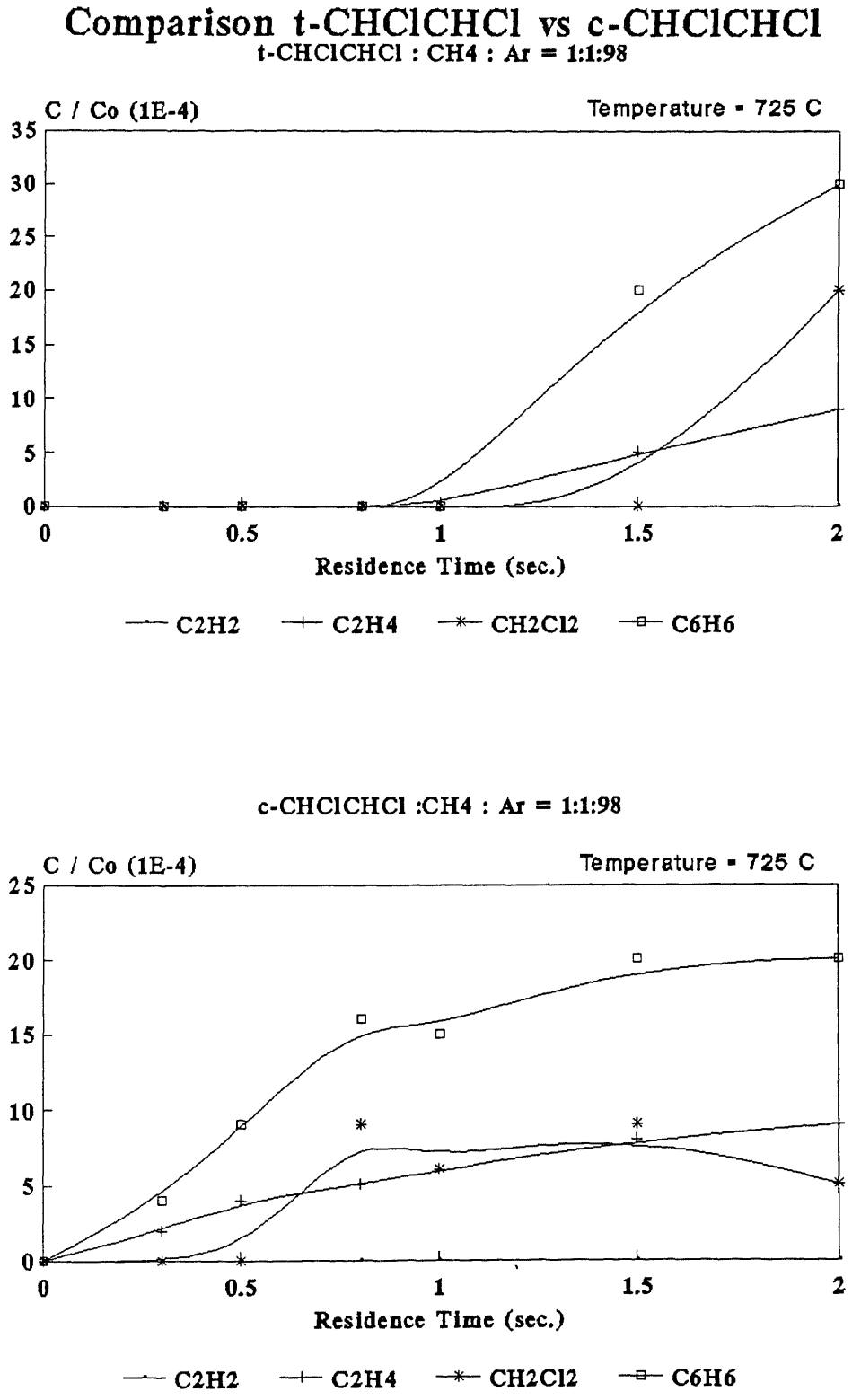

Comparison t-CHClCHCl vs c-CHClCHCl
t-CHClCHCl : CH4 : Ar = 1:1:98
C / Co (1E-4)
Temperature = 725 C
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH2Cl2
C6H6
c-CHClCHCl :CH4 : Ar = 1:1:98
C / Co (1E-4)
Temperature = 725 C
25
20
15
10
5
0
0
0.5
1
1.5
2
Residence Time (sec.)
C2H2
C2H4
CH2Cl2
C6H6

Figure 4.59

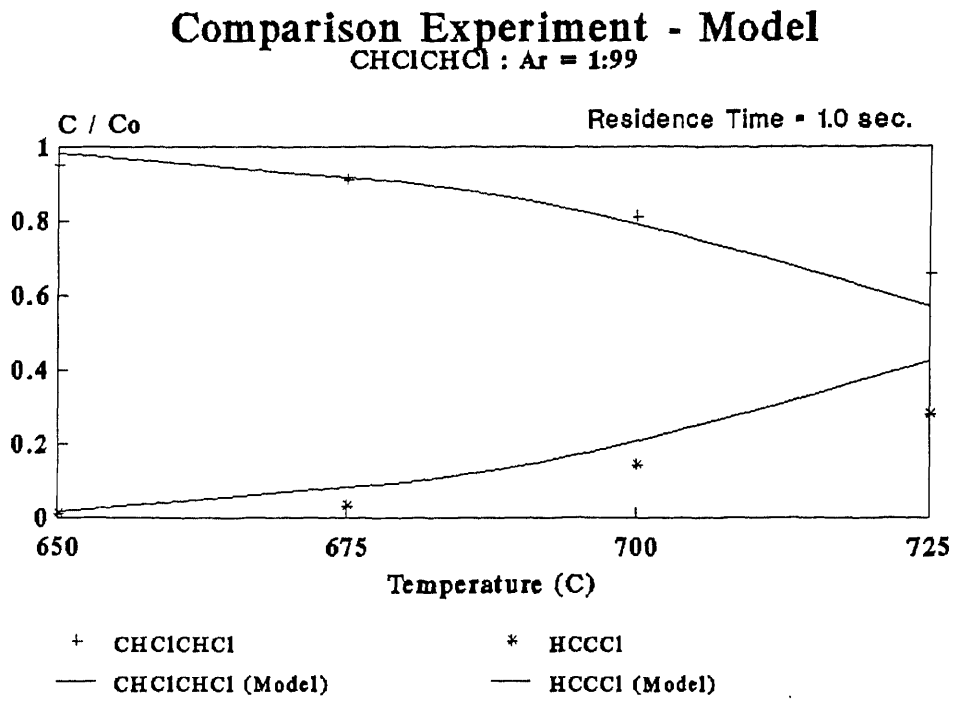


Figure 4.60

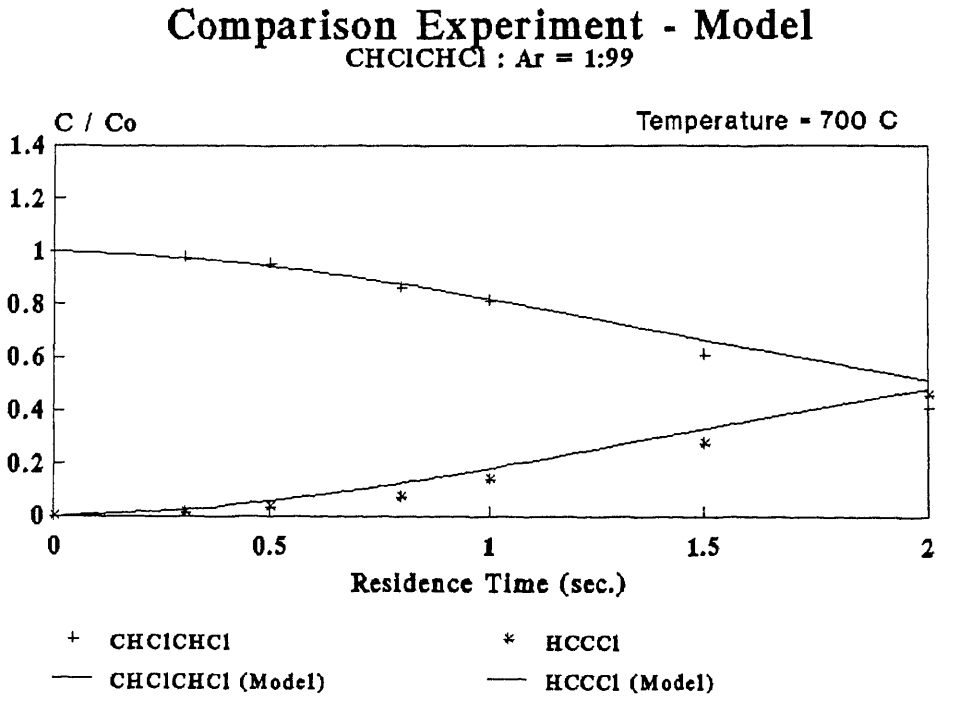


Figure 4.61

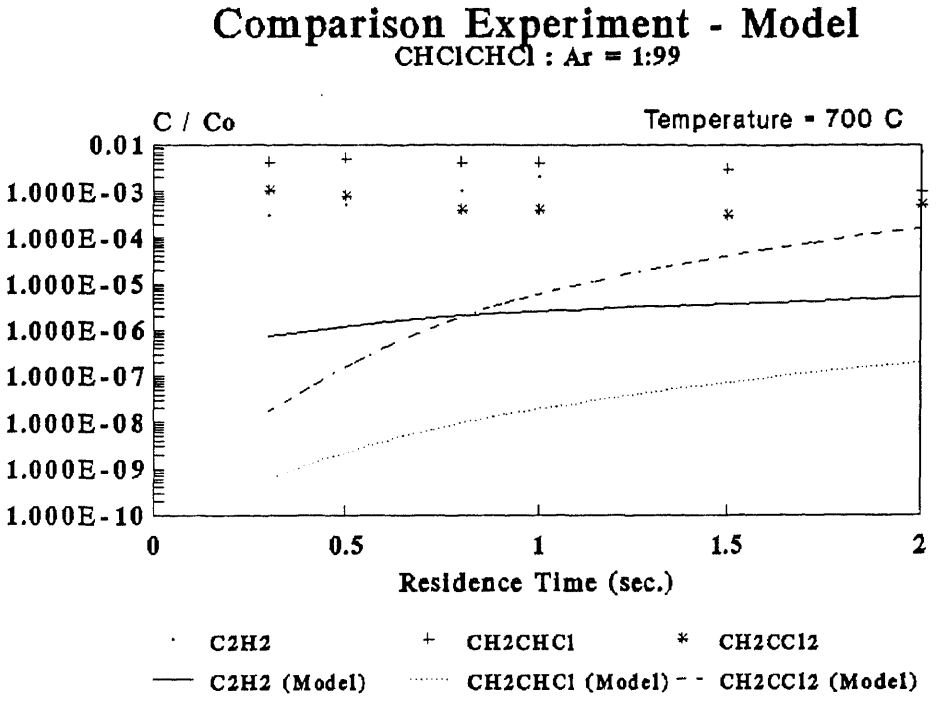


Figure 4.62

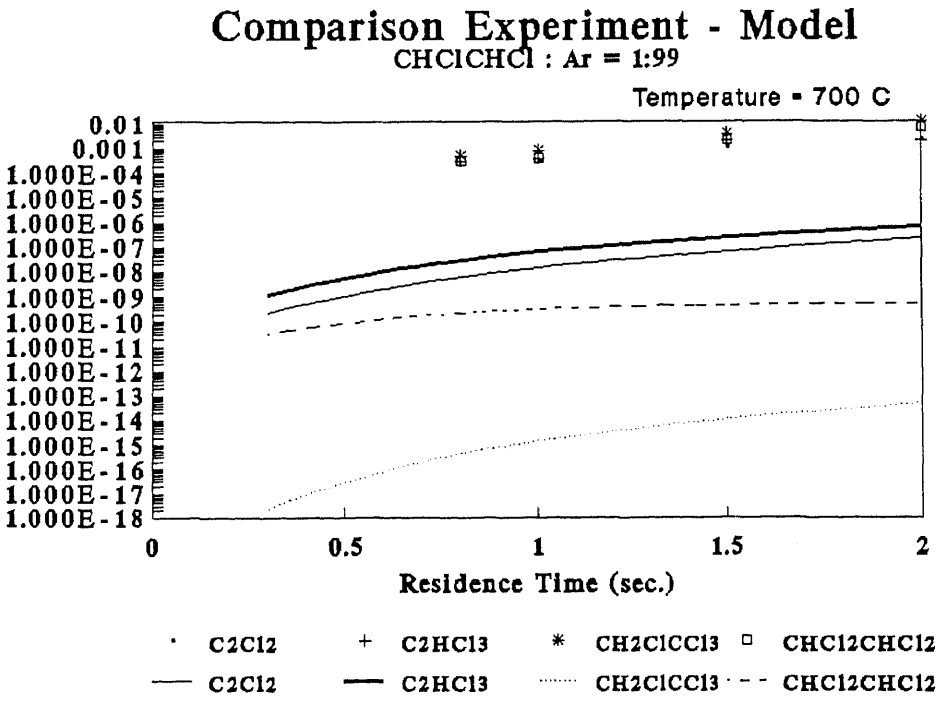


Figure 4.63

CHAPTER 5

CONCLUSION

The thermal reaction of trans-1,2-dichloroethylene (DCEE) in methane and oxygen mixtures in Ar bath gas has been studied in 10.5 mm I.D tubular flow quartz reactors at 1 atmosphere pressure, isothermal over a temperature range from 575°C to 1000°C and a residence time range of 0.3 to 2.0 seconds. The thermal decomposition of six reactant ratio sets is studied to determine important chlorocarbon reaction pathways for testing and developing of the detailed elementary reaction mechanism.

The thermal reaction of trans-1,2-dichloroethylene in the gas phase proceeds predominately via unimolecular HCl elimination under the reaction condition of the present experiments. The C-Cl bond fission is expected to become important at higher temperature, competing with the HCl elimination.

The trans-1,2-dichloroethylene decay and product distribution were different when O_2 and/or CH_4 were present. Increases in O_2 concentration were observed to accelerate reagent loss, especially the fuel lean and stoichiometric systems, relative to the DCEE/CH_4 system. In the DCEE/CH_4/O_2 the major products were C_2H_2, CHCCl, CH_2CHCl, CH_2CCl_2, C_6H_6, CO, CO_2, HCl over a wide temperature range. Minor products were C_2H_4, CH_3Cl, CH_2Cl_2, C_2Cl_2, CH_3CCl_3, C_6H_5Cl, $C_6H_5CH_3$.

The extensive experimental data will be utilized for testing a mechanism consisting of elementary reactions based on thermochemical principles, Transition State Theory and Quantum Rice-Ramsperger-Kassel (QRRK) analysis.

A small reaction mechanism was developed for initial reaction step in DCEE/Ar system. High pressure limit rate constants obtained in this study for the initial decomposition of DCEE were determined to be :

Table 5.1 Rate Constants for CHClCHCl/Ar Pyrolysis

Reaction	A(1/sec)	Ea(Kal/mole)
$CHClCHCl \rightarrow HCCCl + HCl$	1.05E14	69.68
$CHClCHCl \rightarrow CHCHCl + Cl$	3.53E15	89.55

Rate constants for other important reaction :

Table 5.2 Rate Constants for CHClCHCl/Ar Pyrolysis

Reaction	A(1/sec)	Ea(Kal/mole)
$CHClCHCl + HCl \rightarrow CH_2ClCHCl_2$	4.88E11	41.00
$CH_2CCl_2 \rightarrow HCCCl + HCl$	1.05E14	69.81

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